



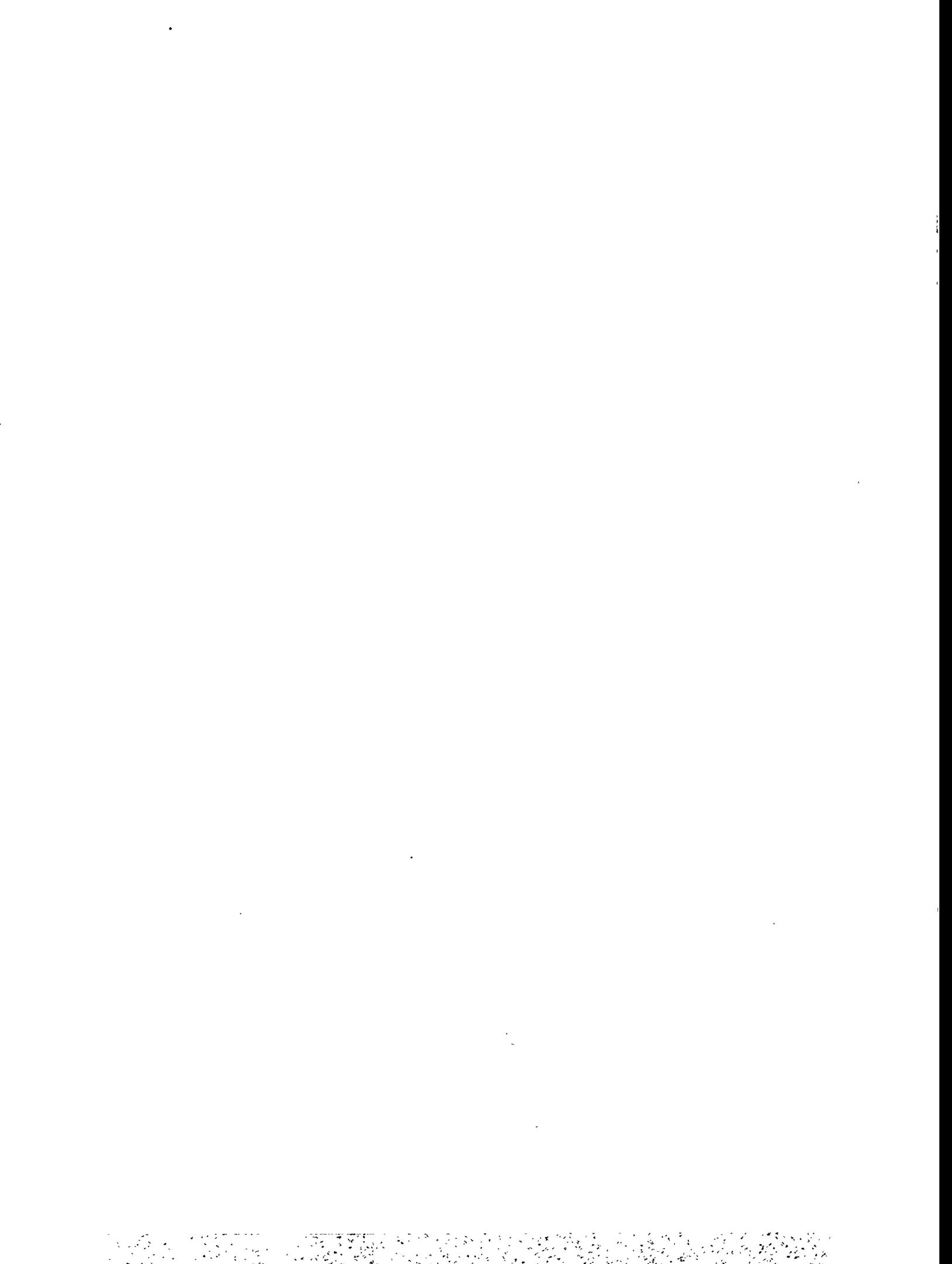
**CHARACTERIZATION
MONITORING &
SENSOR TECHNOLOGY
CROSSCUTTING
PROGRAM**

**Technology Summary
August 1996**

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CHARACTERIZATION, MONITORING, AND SENSOR TECHNOLOGY CROSSCUTTING PROGRAM TECHNOLOGY SUMMARY

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INTRODUCTION

The Office of Environmental Management (EM) is responsible for cleaning up the legacy of radioactive and chemically hazardous waste at contaminated sites and facilities throughout the U.S. Department of Energy (DOE) nuclear weapons complex, preventing further environmental contamination, and instituting responsible environmental management. Initial efforts to achieve this mission resulted in the establishment of environmental restoration and waste management programs. However, as EM began to execute its responsibilities, decision makers became aware that the complexity and magnitude of this mission could not be achieved efficiently, affordably, safely, or reasonably with existing technology.

Once the need for advanced cleanup technologies became evident, EM established an aggressive, innovative program of applied research and technology development. The Office of Technology Development (OTD) was established in November 1989 to advance new and improved environmental restoration and waste management technologies that would reduce risks to workers, the public, and the environment; reduce cleanup costs; and devise methods to correct cleanup problems that currently have no solutions.

In 1996, OTD added two new responsibilities—management of a Congressionally mandated environmental science program and development of risk policy, requirements, and guidance. OTD was renamed the Office of Science and Technology (OST).

THE EM ORGANIZATION

OST is one of seven Deputy Assistant Secretarial Offices within EM. Each Deputy Assistant Secretarial Office is discussed here, with the exception of OST (EM-50), addressed in detail later in this Introduction.

Office of the Assistant Secretary for Environmental Management (EM-1)

The Office of the Assistant Secretary for Environmental Management provides centralized direction for waste management operations, environmental restoration, and related applied research and development programs and activities within DOE. The Office of the Assistant Secretary develops EM program policy and guidance for the assessment and cleanup of inactive waste sites and facilities, and waste management operations; develops and implements an applied waste research and development program to provide innovative environmental technologies to yield permanent disposal solutions at reduced costs; and oversees the transition of contaminated facilities from various departmental programs to environmental restoration. The Assistant Secretary provides guidance to all DOE Operations Offices. Organizational relationships are shown in Figure A.

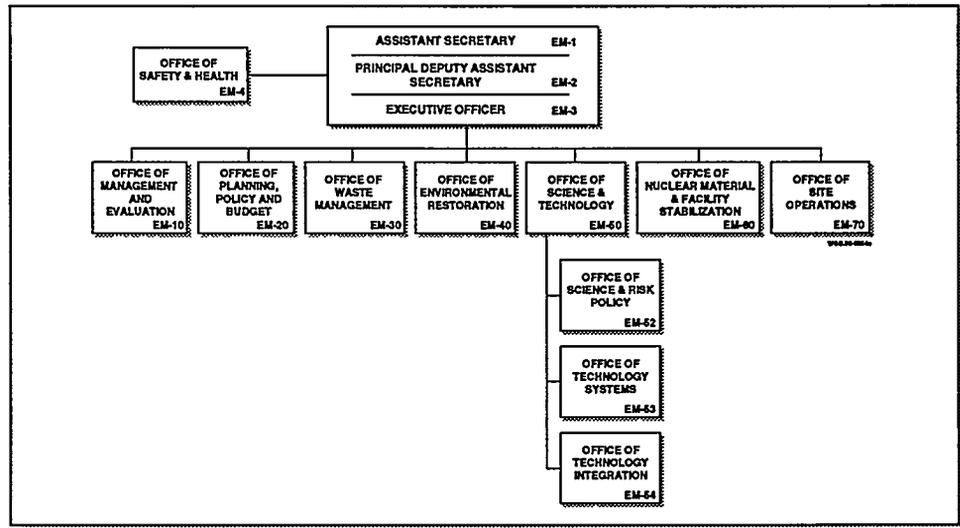


Figure A. Office of Environmental Management Organization Chart

The Office of Management and Evaluation (EM-10)

The Deputy Assistant Secretary for Management and Evaluation serves as the Assistant Secretary’s principal advisor on all administrative functions and activities for EM line offices. Responsibilities include personnel administration; training and career development; total quality management; organization and manpower management; cost and performance management; space and logistics management; acquisition, procurement, and contracts management; general administrative support services; and automated data processing, automated office support systems, and information resources management.

The Office of Planning, Policy, and Budget (EM-20)

The Office of Planning, Policy, and Budget analyzes and provides support on policy and planning issues associated with environmental compliance and cleanup activities, waste management, nuclear materials and facilities stabilization, overall budget and priority setting analyses, nuclear nonproliferation policy practices, and the ultimate disposition of surplus materials and facilities. This Office is also responsible for the review, coordination, and integration of inter-site, interagency and international planning activities related to these issues. The Office coordinates policy and procedural issues associated with the external regulation of the environmental restoration, waste management, and nuclear materials and facility stabilization programs.

The Office of Waste Management (EM-30)

The Office of Waste Management provides an effective and efficient system that minimizes, treats, stores, and disposes of DOE waste as soon as possible in order to protect people and the environment from the hazards of those wastes. The Office carries out program planning and budgeting, evaluation and intervention, and representation functions associated with management

of radioactive high-level, transuranic, and low-level waste; hazardous and sanitary waste; and mixed waste.

The Office of Environmental Restoration (EM-40)

The Office Environmental Restoration remediates departmental sites and facilities to protect human health and the environment from the risks posed by inactive and surplus DOE facilities and restores contaminated areas for future beneficial use. This Office provides program direction for and management of environmental restoration activities involving inactive sites and facilities, including the decontamination of surplus facilities.

The Office of Nuclear Material and Facility Stabilization (EM-60)

The Nuclear Material and Facility Stabilization program mission is to protect people and the environment from the hazards of nuclear materials and to deactivate surplus facilities in a cost-effective manner. The Office provides program planning and budgeting, evaluation and intervention, and representation functions associated with the stabilization of nuclear materials and the deactivation of surplus facilities.

The Office of Site Operations (EM-70)

Acting to eliminate barriers and ensure that field concerns are recognized in major EM decisions, the Office of Site Operations as a focal point and champion for the Operations Offices and field sites, serving as facilitator, coordinator and ombudsman for crosscutting issues and topics raised by the various EM elements. The Office of Site Operations provides Headquarters policy direction for landlord planning and budgeting and sets policy and guidance to improve the effectiveness of crosscutting environment, transportation management, and waste minimization activities.

THE OFFICE OF SCIENCE AND TECHNOLOGY (EM-50)

OST manages and directs focused, solution-oriented national technology development programs to support EM by using a systems approach to reduce waste management life-cycle costs and risks to people and the environment. OST programs involve research, development, demonstration, testing, and evaluation of innovative technologies and technology systems that meet end-user needs for regulatory compliance. Activities include coordination with other stakeholders and the private sector, as well as collaboration with international organizations. In 1994, the EM program identified five major problem areas on which to focus its technology development activities, and implemented Focus Areas to address these problems. In addition, some needs were identified that were common to all the Focus Areas, and three Crosscutting Programs were created to address them.

OST programs establish, manage, and direct targeted, long-term research programs to bridge the gap between broad fundamental research that has

wide-ranging application and needs-driven applied technology development research. OST expects to produce technologies to answer the needs of its major customers within EM for innovative science and technology through

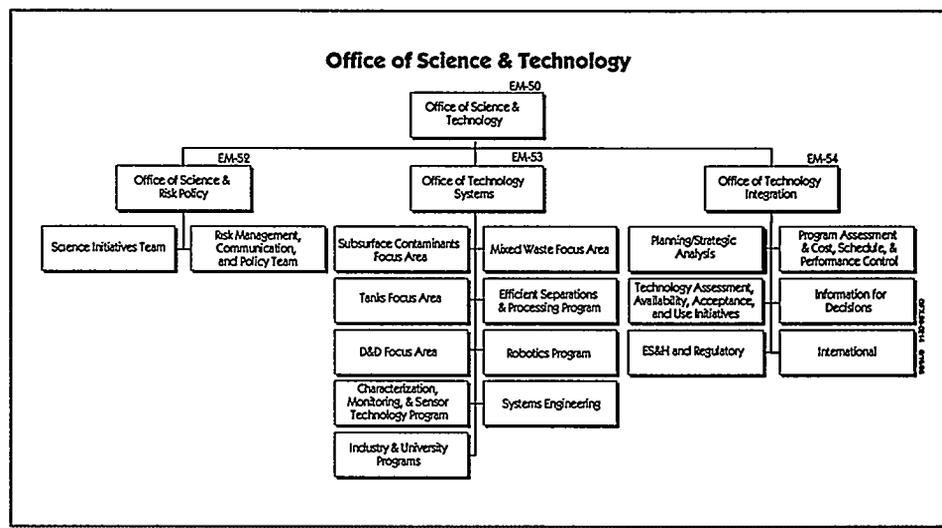


Figure B. Organization Chart of the Office of Science and Technology

integration of basic research programs, applied research programs (Focus Areas and Crosscutting Programs), industry partnerships, and technology transfer activities.

Three offices comprise OST: the Office of Science and Risk Policy, the Office of Technology Systems, and the Office of Technology Integration. The organization for OST is shown in Figure B.

OFFICE OF SCIENCE AND RISK POLICY (EM-52)

The Office of Science and Risk Policy manages EM's Science Program and the formulation of risk policy. The mission of this office includes the development of a targeted, long-term basic research agenda for environmental problems so that "transformational" or breakthrough approaches can lead to significant reduction in the costs and risks associated with the EM Program. This Office also bridges the gap between broad fundamental research that has wide-ranging applicability, such as that performed in DOE's Office of Energy Research, and needs-driven applied technology development that is conducted in EM's Office of Technology Systems. This Office was designed to focus the country's science infrastructure on critical national environmental management problems.

The Science Program draws on information from its DOE customers to identify necessary basic research. The Science Program concentrates its efforts on the characterization of DOE's wastes and contaminants, interactions of

radioactive elements with biosystems in various natural media and waste forms, extraction and separation of radioactive and hazardous chemical contaminants, prediction and measurement of contaminant movement in DOE facilities' environments, and formulation of scientific bases for the risks associated with DOE-based contaminants.

Risk policy activities within this Office involve the development of policies, procedures, and guidance to ensure that EM activities in preventing risks to the public, workers, and the environment are within prescribed, acceptable levels. Risk evaluation methods and event and consequence analyses provide DOE with a basis for assessing both the risk and any actions being considered to reduce that risk. The Office of Science and Risk Policy ensures that advances in risk evaluation methods are integrated into coherent decision-making processes regarding risk acceptability. Decision-making processes must meet DOE missions while protecting public health, worker health and safety, ecosystem viability, and cultural and national resources.

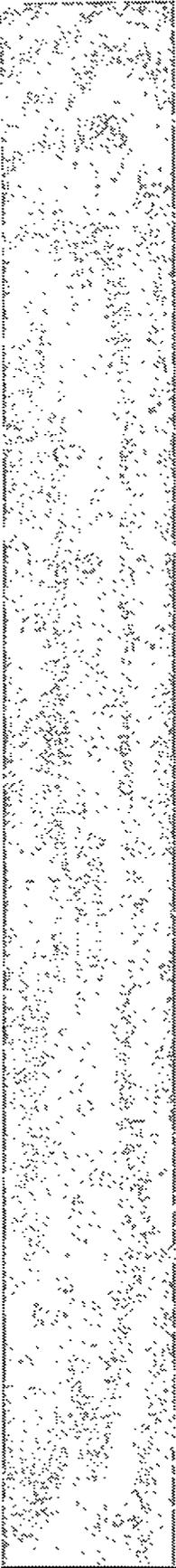
OFFICE OF TECHNOLOGY SYSTEMS (EM-53)

OST programs involve research, development, demonstration, testing, and evaluation activities designed to produce innovative technologies and technology systems to meet national needs for regulatory compliance, lower life-cycle costs, and reduced risks to the environment. To optimize resources, OST has streamlined technology management activities into a single focus team for each major problem area. To ensure programs are based upon user needs, these teams include representatives from user offices within EM. There are five major problem areas upon which technology development activities are focused on five major problem areas.

- Mixed Waste Characterization, Treatment, and Disposal
- Radioactive Tank Waste Remediation
- Contaminant Plume Containment and Remediation
- Landfill Stabilization
- Decontamination and Decommissioning

Mixed Waste Characterization, Treatment, and Disposal Focus Area

DOE stores 167,000 cubic meters of mixed low-level and transuranic waste from over 1,400 mixed radioactive and hazardous waste streams at 38 sites. The Mixed Waste Characterization, Treatment, and Disposal Focus Area provides an integrated, multi-organizational, national team to develop treatment systems for the department's inventory of mixed radioactive and hazardous waste and to dispose of these low-level and transuranic waste streams in a manner that regulatory requirements.



This Focus Area plans to demonstrate three technologies to treat at least 90 percent of DOE's stored mixed waste inventory by the end of FY97. The outcome will be waste forms that are reduced in volume, as compared to the volume of stored mixed waste and meet regulatory requirements for safe, permanent disposal. Technology development is being conducted in the areas of thermal and nonthermal treatment emissions, nonintrusive drum characterization, material handling, and final waste forms.

Radioactive Tank Waste Remediation Focus Area

The Radioactive Tank Waste Remediation Focus Area develops technologies to safely and efficiently remediate over 300 underground storage tanks that have been used to process and store more than 100 million gallons of high-level radioactive and chemical mixed waste. Technologies are needed to characterize, retrieve, and treat the waste before radioactive components are immobilized. All this must be done in a safe working environment. Emphasis is placed on in situ or remotely handled processes and waste volume minimization.

Research and development of technologies in this area is aimed at enabling tank farm closure using safe and cost-efficient solutions that are acceptable to the public and that fulfill Federal Facility Compliance Act requirements of site regulatory agreements.

Contaminant Plume Containment and Remediation Focus Area *

More than 5,700 DOE groundwater plumes have contaminated over 600 billion gallons of groundwater and 50 million cubic meters of soil. The Contaminant Plume Containment and Remediation Focus Area is developing technologies to address environmental problems associated with hazardous and radioactive contaminants in soil and groundwater that exist throughout the DOE complex, including radionuclides, heavy metals and dense, non-aqueous phase liquids and plumes of organic contaminants. Migration of some contaminants threatens water resources, and in some cases has already had an adverse impact on the off-site environment. Technology developed within this specialty area provides effective methods to contain contaminant plumes and new or alternative technologies for remediating contaminated soils and groundwater. Emphasis is placed on the development of in situ technologies to minimize waste disposal costs and potential worker exposure by treating plumes while still in the subsurface. Containment technologies are being developed in conjunction with the Landfill Stabilization Focus Area, since it fulfills similar technical needs.

Landfill Stabilization Focus Area *

Landfills at DOE facilities contain more than three million cubic meters of radioactive and hazardous buried waste, some of which has been migrating to the surrounding soils and groundwater. These landfills require remediation to reduce environmental and societal risks posed by these migrating

contaminants. The mission of this Focus Area is to develop and demonstrate more cost-effective, environmentally sensitive, and safer technologies that satisfy DOE customer needs for source term containment, remediation, and management of landfills.

The emphasis for this Focus Area is on technologies that provide new and/or improved capabilities for landfill containment and in situ stabilization, non-intrusive characterization of sites and waste, retrieval and treatment systems, verification and monitoring systems, and improved disposal systems. A major goal is to demonstrate by January 1997 the ability to contain or stabilize 90 percent of source terms at DOE's contaminated sites, preventing further migration.

** In mid-1996, the Contaminant Plume Containment and Remediation Focus Area and the Landfill Stabilization Focus Area were combined into one Focus Area, however, they are being treated as separate areas in the 1996 Technology Summaries. The program is expected to benefit greatly from this efficient use of resources since both Focus Areas are working to solve similar problems.*

Decontamination and Decommissioning Focus Area

The Decontamination and Decommissioning Focus Area is developing technologies to solve the department's challenge of deactivating 7,000 contaminated buildings and decommissioning 700 contaminated buildings. It is also responsible for decontaminating the metal and concrete within those buildings and disposing of 180,000 metric tons of scrap metal. Technology development for decontamination and decommissioning focuses on large-scale demonstrations, each of which incorporates improved technologies identified as responsive to high-priority needs. All technologies will be considered for eventual deployment, and side-by-side comparisons of improved technologies are being performed using existing commercial technologies as baselines.

CROSSCUTTING PROGRAMS

In addition to work directed to specific Focus Areas, EM is engaged in research and development programs that cut across these problem areas. Technologies from these Crosscutting Programs may be used within two or more of the Focus Areas to help meet program goals. These programs complement and facilitate technology development in the Focus Areas as shown in Figure C. The Crosscutting Programs are:

- Characterization, Monitoring, and Sensor Technologies,
- Efficient Separations and Processing, and
- Robotics Technology Development Program.

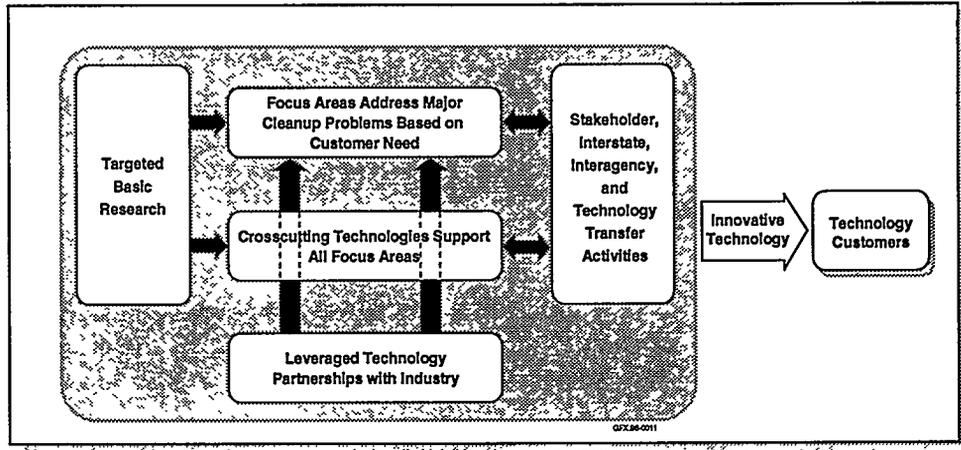


Figure C. Relationships between Focus Areas and Crosscutting Programs

Characterization, Monitoring, and Sensor Technologies Crosscutting Program

DOE is required to characterize more than 3,700 contaminated sites, 1.5 million barrels of stored waste, 385,000 m³ of high-level waste in tanks, and from 1,700 to 7,000 facilities before remediation, treatment, and facility transitioning commence. Monitoring technologies are needed to ensure worker safety and effective cleanup during remediation, treatment, and site closure.

Efficient Separations and Processing Crosscutting Program

Separations and selected treatment processes are needed to treat and immobilize a broad range of radioactive wastes. In some cases, treatment technologies do not exist; in others, improvements are needed to reduce costs and secondary waste volumes and to improve waste form quality. This Crosscutting Program concentrates efforts on specific high-priority needs as defined by the Focus Areas, then evaluates and adapts the technologies for other applicable Focus Areas.

This program is working to meet Federal Facilities Compliance Act milestones and other regulatory requirements, and to develop separations and treatment technologies that minimize risk, the volume of waste requiring deep, geological disposal, and secondary waste volumes.

Robotics Technology Development Crosscutting Program

Existing technologies are often inadequate to meet EM's mission needs both at a reasonable cost and under conditions that promote adequate worker safety. Robotic systems reduce worker exposure to the absolute minimum while providing proven, cost-effective, and, in some cases, the only acceptable approach to problems.

Robotics remote systems development work occurs in three areas. Remote systems for decontamination and dismantlement of facilities will reduce or eliminate extensive worker radiation protection requirements and increase

productivity. Robotic systems for characterization and retrieval of stored tank waste will allow work to proceed within the radiation fields in the waste storage area. Automated chemical/radiological analysis systems are estimated to provide a cost benefit of \$10.5 billion from FY96 through FY00.

INDUSTRY AND UNIVERSITY PROGRAMS

Although not a Focus Area or Crosscutting Program, one additional internal activity should be discussed since it is an integral part of solving the problems addressed by OST.

Industry and University Programs work to involve private sector stakeholders such as users, regulators, public interest groups, commercial parties, sites, and universities in developing and implementing improved technologies that address the needs of the Focus Areas. The programs work with interested parties in assessing the acceptability, availability, and use of improved technical solutions by providing uniform guidance, tools, and initiatives, as well as technology transfer processes, and ensure that the needs of stakeholders are integrated into decision-making processes.

Industry activities support 80 contracts with the private sector; and university activities support international programs, the Small Business Innovative Research Program, as well as various Focus Areas. Industry and university activities are supported through the direct government contracting mechanisms discussed in the "DOE Business Opportunities" section.

OFFICE OF TECHNOLOGY INTEGRATION (EM-54)

The Office of Technology Integration addresses issues that affect the involvement of critical external entities such as production/waste sites, users, the public, tribes, regulators, and commercial parties. The office is involved in the assessment, acceptability, availability, and use of improved technical solutions by providing uniform guidance, tools, and initiatives to support the Office of Technology Systems. This office also sponsors efforts to encourage and promote the involvement of affected parties' in regulatory issues.

In addition, the Office of Technology Integration sponsors domestic and international technology transfer programs within OST and coordinates planning and cost-benefit analyses with other EM organizations.

CHARACTERIZATION, MONITORING, AND SENSOR TECHNOLOGY CROSSCUTTING PROGRAM OVERVIEW

PURPOSE

The purpose of the Characterization, Monitoring, and Sensor Technology Crosscutting Program (CMST-CP) is to deliver appropriate characterization, monitoring, and sensor technology (CMST) to the Office of Waste Management (EM-30), the Office of Environmental Restoration (EM-40), and the Office of Facility Transition and Management (EM-60).

In addition to being appropriate for EM-30/40/60s needs, the technology development must be cost effective. Furthermore, the required technologies must be delivered and implemented when needed. Accordingly, and to ensure that available DOE and other national resources are focused on the most pressing needs, management of the technology development is concentrated on the following Focus Areas:

- I. Mixed Waste Characterization, Treatment, and Disposal
- II. High-Level Waste Tank Remediation
- III. Contaminant Plume Containment and Remediation
- IV. Landfill Stabilization
- V. Decontamination and Decommissioning,

TECHNOLOGY NEEDS

The EM mission cannot proceed intelligently, safely, or economically unless the problems it addresses and the processes it employs are adequately characterized or monitored. A common problem is that the costs of characterization and monitoring technologies are unacceptably high. Another is that critical characterization, monitoring, and sensor technologies needed to address several of the most important EM problems are not available, are not yet accepted by regulators, or have not been proven under EM mission conditions. Examples of needed characterization, monitoring, and sensor technologies are listed below, by Focus Area.

Plumes Focus Area: Instrumentation and methods for determination of the location, nature, level, and 3-dimensional extent of Dense Non-Aqueous Phase Liquids (DNAPLs) in the subsurface; sensors and instrumentation for subsurface deployment by cone penetrometer or other minimally intrusive methods for determination of metal and radioactive contaminants.

Tanks Focus Area: In situ sensor systems for determination of physical properties, gross matrix characteristics, and chemical constituents of tank waste; sensor deployment systems, including cone penetrometer sensor systems to deploy into tank waste and novel remote sensing deployment systems such as fiber-optic laser systems; on-line process monitors and controls for retrieval, transfer, and treatment operations.

Mixed Waste Focus Area: Safe, fast, and economical instrumentation and methods for characterization and monitoring of mixed waste in containers and mixed waste treatment processes, effluents, and final waste forms—for assurance of worker, public, process, and facility safety, and to assure the quality and public acceptance of treatment processes and final waste forms.

Landfill Stabilization Focus Area: Instrumentation and methods for establishing and monitoring the integrity of subsurface barriers; non-intrusive geophysical methods to characterize and locate buried waste, buried structures, waste zones, and geologic structures.

Decontamination and Decommissioning: Sensors and instrumentation for non-destructive assay of Resource Conservation and Recovery Act (RCRA) metals and radionuclides in process equipment, ducts, pipes, and soils; technologies for real-time monitoring of the progress and quality of decontamination.

All the Focus Areas have characterization and monitoring development needs; therefore technology that is developed for one Focus Area can often be adapted to solve problems in another. The CMST-CP identifies technology gaps, integrates technology development, and leverages resources to achieve synergy in development and to provide cost-effective solutions. The resources include those of other federal agencies, private companies, and universities as well as those within the DOE. The CMST-CP promotes collaboration with other federal agencies through interagency agreements (IAGs). Private sector R&D involvement is promoted through Cooperative Research and Development Agreements (CRADAs), Program Research and Development Announcement (PRDA), Research Opportunity Announcements (ROAs), the Small Business Innovation Research (SBIR) program, and the Technology Reinvestment Project (TRP). The CMST-CP provides necessary coordination to achieve timely and cost-effective development and implementation of needed characterization, monitoring, and sensor technologies.

WINDOWS OF OPPORTUNITY FOR THE CMST-CP

Characterization, monitoring, and sensor technology is needed throughout the EM process. The functional needs include:

- Initial location and characterization of wastes and waste sites before treatment

- Monitoring of waste retrieval and remediation processes
- Characterization and monitoring of waste treatment processes, products, and effluents
- Site closure and long-term compliance monitoring

The priorities and schedules for CMST development and implementation must conform to the directions and needs specified by the Focus Areas.

ACCOMPLISHMENTS

- The CMST-CP currently supports technology development projects in all five Focus Areas. The CMST needs statements in the solicitations for PRDA, ROA, and SBIR grant applications were developed by CMST-CP team members who worked closely with representatives of the Focus Area Management Teams and other customer representatives to discern and describe the Focus Area needs. The needs statements were subsequently reviewed and validated by the Site Technology Coordination Groups (STCGs) and DOE authorities.
- Representatives from the five Focus Areas were invited to participate in the CMST-CP Program Meeting. Activities included their presentations on CMST needs, principal investigator (PI) presentations, and a panel session on plans for technology transfer and commercialization.
- At the Program Meeting, the CMST-CP conducted expert technical and customer reviews of 27 FY95 CMST-CP projects. Each was reviewed by three technical experts and two to four Focus Area representatives. (The review team consisted of 21 technical reviewers and 10 Focus Area representatives.) About 110 people attended. The evaluation information was transmitted to the PIs through the Technical Program Officers (TPOs) and Technical Program Managers (TPMs).
- The Tanks Focus Area (TFA) and the CMST-CP jointly evaluated 54 proposals received in response to the August 1995 joint Call for Proposals for CMST development. The CMST-CP provided technical evaluators; the TFA provided evaluators representing users' needs at the Savannah River and Hanford Sites. Three representatives of the Mixed Waste Focus Area (MWFA) also served as user needs evaluators. The evaluation produced a consensus recommendation of five proposals for FY96 funding.
- The CMST-CP conducted an expert technical and customer review of CMST-CP funded FY95 and proposed FY96 characterization/monitoring work at the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University (MSU), Starkville, Mississippi. The projects and proposals were evaluated September 13 and 14, 1995, at MSU by technical peers and Focus Area customer representatives.

- CMST-CP staff provided technical input for review of 26 new CMST tasks proposed for funding by the Landfill Stabilization Focus Area (LSFA) and MWFA. The input was provided to the Landfill and Mixed Waste Implementation Teams.
- CMST-CP staff participated in the expert technical evaluation of 40 CMST proposals received in response to the Morgantown Energy Technology Center (METC) ROA solicitation entitled "Applied Research and Development of Technologies for Environmental Restoration and Waste Management II."
- CMST-CP staff participated in the expert technical evaluation of 52 CMST proposals received in response to the METC PRDA solicitation entitled "Characterization, Monitoring, and Sensor Technology (CMST) Development."
- CMST-CP staff coordinated the review of 20 SBIR grant applications received in response to the FY95 solicitation topic entitled, "Characterization, Monitoring, and Sensor Technologies for Radioactive and Hazardous Waste." In addition, they either provided or arranged for expert technical reviews of numerous Phase I ROA and SBIR reports and Phase II extension proposals.
- CMST-CP staff reviewed abstracts of and submitted scoring sheets for 59 papers submitted for presentation at the Technology Information Exchange (TIE) workshop, April 16 to 18, 1995 in Santa Fe, New Mexico.
- CMST-CP staff served on the Rapid Commercialization Initiative (RCI) peer review panel for the monitoring and assessment technology category and reviewed 10 proposals submitted in response to the RCI Announcement issued August 16.
- The CMST-CP sponsored Expedited Site Characterization (ESC) at the DOE Pantex Plant Zone 12 Groundwater Investigation and Savannah River D-Area Oil Seepage Basin sites.

CMST-CP PERSONNEL PARTICIPATED IN

1. Development of the "Mixed Waste Characterization Reference Document"
2. A workshop on Non-Destructive Assay/Non-Destructive Evaluation (NDA/NDE) technology development projects funded by EM-50
3. Development of the "Environmental Science and Technology Strategic Plan, 1996-2005"
4. Site visits with Focus Area team members to collect information about site technology needs and schedule requirements

The CMST-CP has distributed the CMST Progress Report, a monthly compilation of the technical progress reports from all CMST-CP projects since November 1993. With the cooperation and assistance of METC personnel, the progress report has also included reports from CMST projects funded through PRDA and ROA activities since October 1994. This is part of a continuing effort to disseminate information about CMST development activities to potential customers.

TECHNOLOGY COLLABORATION/TRANSFER

The CMST-CP technology transfer roadmap consists of six main sections: needs assessment, identification of technologies for transfer, a managing-technology-for-development (MTD) process, a technology de-risking process, a technology verification (and/or certification) process, and a "hands-on" technical assistance process. Through the use of this roadmap process, many barriers that impede acceptance of new technologies have been identified and mitigated.

CMST-CP staff organized a workshop and forum on Chemical Sensors for Environmental Applications. The preliminary results of a market study on existing technologies and users' needs were presented both at the two-day workshop and at the afternoon forum. The market study was commissioned to Unimar, a marketing research firm that was one of 14 respondents to a related request for proposals. The workshop was held immediately prior to the Pittsburgh Conference in Chicago. More than 80 users, developers, and manufacturers of chemical sensors and field deployable analytical instrumentation participated, dealing with issues concerning developing, adapting, and commercializing analytical instrumentation technologies for environmental analysis. The objectives of the workshop and forum were to:

- Identify existing sensor technologies appropriate for EM field deployable environmental analysis and sensing
- Determine the present and potential market demand for commercial field deployable environmental analysis instrumentation
- Publicize, as widely as possible, market information relevant to commercial field deployable environmental analysis instrumentation
- Encourage the redirection of existing technologies or the development of innovative technologies as commercial products for field deployable environmental analysis

The CMST-CP provided support for beta-site testing of the Sandia Robust Hydrogen Sensor at Hanford for monitoring high-level tank headspace gas. The sensor achieved faster response and higher sensitivity than the current practice; however, it failed to meet the ruggedness requirement. Sandia

National Laboratory (SNL) is working with a commercialization partner to improve the product packaging and design.

The CMST-CP, jointly with the EPA Consortium for Site Characterization Technologies (CSCT), sponsored the "RCRA and Other Heavy Metals in Soils Demonstration." This activity was organized by MSE, Inc., the prime contractor for the DOE Western Environmental Technology Office; Sandia National Laboratory, a technology verification entity under contract to the CSCT; and the Ames CMST-CP and Technology Transfer projects office. Four technology developers participated in the field demonstration activities during the week of September 25, 1995, in Butte, Montana. Split samples were archived and sent to two EPA laboratories for confirmatory analyses. The final evaluation report, scheduled to be issued by the EPA in March-April 1996, will not only detail the performance (and cost of performance) of demonstrated technologies against individual developer or vendor claims, but also comparatively evaluate these field performance data with results gained from using baseline, laboratory EPA methods. The performance of the four technologies under differing matrices and test conditions will be documented in accordance with a well-defined quality assurance/quality control (QA/QC) data protocol.

The CMST-CP is also pursuing the opportunity to participate in the "Rapid Commercialization Initiative," a coordinated effort between the Department of Commerce, Department of Defense, EPA, and DOE. In addition, verification activities dealing with continuous emissions monitoring technologies for the detection of heavy metals and volatile organic compounds (VOCs) are being planned.

The CMST-CP provided exhibits for the following meetings:

- Interagency exhibit sponsored by the U.S. Senate Environment and Public Works committee
- International Symposium and Trade Fair on the Cleanup of Manufactured Gas Plants, Prague

Recent Presentations and Publications include the following:

E. Lightner and C. Purdy, "Cone Penetrometer Development and Testing for Environmental Applications," *Proceedings of the CPT '95 Symposium*, Sweden, (1995).

Glenn Bastiaans, "The Department of Energy Office of Environmental Management's Role in the Development of Chemical Sensors for the Environment," presented at the 188th Meeting of the Electrochemical Society, (October, 1995).

P. Wang, T. A. Zachry, M. S. Anderson, and J. B. Paladino, "Roadmap Process for Commercialization and Use of Emerging Characterization and Monitoring Technologies," to be published in the *Proceedings of Waste Management '96*.

W. Haas and N. B. French, "A Survey of Continuous Emissions Monitoring Technologies for Volatile Organic Compounds, HCl, and Ammonia," Presented at the 1996 International Conference on Incineration and Thermal Treatment Technologies, (May, 1996).

P. Wang, C. Purdy, and E. Lightner, "Emerging Technologies for Environmental Characterization and Monitoring," *Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, Spectrum '96*, (August, 1996).

FUTURE DIRECTIONS

Knowledge and understanding of the CMST needs of the Focus Areas are critical for success. Hence, the CMST-CP will continue to concentrate on establishing excellent communication with the STCGs and the Focus Area Management and Implementation Teams. Future activities will be influenced more by the specific needs of site technology customers and stakeholders, and less by the interests and capabilities of technology developers.

The chief technical responsibility of the CMST-CP will continue to be development and implementation of new and emerging CMST applicable to EM needs. Near-term thrusts will include:

- Promotion of ESC, including multidisciplinary ESC teams in the private sector
- Field usable sensors and systems integrated with non-invasive tools for real-time determination of chemical/physical properties in the subsurface
- In situ sensors to determine spatial variability of chemical/physical properties of tank waste content
- Sensor technologies to support HLW retrieval and immobilization operations; continuous monitoring technologies for offgas and effluent streams to ensure optimized treatment process control
- Front-end characterization of containerized wastes for treatment; on-line sensors for real-time monitoring of chemical/radioactive contaminants during decontamination operations
- Development of more effective teaming with the DoD, EPA, and other government agencies with interests in CMST

In accordance with the best available information from the Focus Area Management and Implementation Teams and the STCGs, the CMST-CP will attempt to deliver required new technologies and technology improvements, when needed, through coordinated and focused development efforts in the DOE as well as in other federal agencies, the private sector, and universities. The goal is rapid development and effective application of CMST needed for the EM mission.

The remainder of this document contains brief descriptions of CMST-CP projects funded in FY95. Please see the METC *Technology Summary* and the *Innovative Investment Area (IIA) Technology Summary* for information on other EM-50 projects related to characterization, monitoring, and sensor technologies. Detailed information on any project can be obtained by contacting the PI. Contact information is provided in each project summary.

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1.0

PROJECTS FOR THE CONTAMINANT PLUMES CONTAINMENT AND REMEDIATION FOCUS AREA

The key characterization problem areas needing innovative technologies for Plumes Focus Area include: detection and monitoring of subsurface contaminants in soils and groundwater; location and spatial extent of dense nonaqueous phase liquids (DNAPL) in the subsurface; groundwater flow and contaminant transport modeling to better assess risk of numerous contaminant plumes in soils and groundwater; and characterization and sampling strategies for more technically defensible and cost-effective site characterization.

Nine technologies addressing these problems are currently under development within CMST-CP and many other technologies have been demonstrated and are undergoing commercialization or implementation at DOE sites.

Subsurface sensors under development include: surface acoustic wave (SAW) sensor, able to be deployed down-well for improved measurement of hazardous volatile organic compounds (VOC); an array of SAW sensors for improved resolution of multiple hazardous volatile organic compounds in soil gas and groundwater; chemical flow probe, deployable down-well, using changeable reagent chemistries for detection of metals and organic compounds; Cone Penetrometer Truck (CPT) sampling devices allowing determination of volatile and semi-volatile contaminants at the cone tip while the CPT rod is still in the ground; testing of several CPT sensors and monitors at the Savannah River Site (SRS); and an improved methodology for site characterization achieving great cost and time savings, currently undergoing implementation throughout the DOE complex.

Projects to improve groundwater flow and contaminant transport modeling include: local and regional modeling of contaminant transport throughout the Siberian Basin in Russia with years of groundwater sampling data for model validation, and several geophysical techniques at Box Canyon on the Idaho National Engineering Laboratory (INEL) site for improved understanding of transport through fractured rock (applicable at several sites including INEL, Hanford, and Oak Ridge National Laboratory [ORNL]).

Finally, the induced polarization technique is under development to noninvasively map DNAPLs in the subsurface.

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1.1

INTEGRATION OF INNOVATIVE EXPEDITED SITE CHARACTERIZATION TECHNIQUES

TECHNOLOGY NEED

Because technology gaps exist, even within the context of Expedited Site Characterization (ESC) the scope of this project will involve the use of both state-of-the-practice technologies (SOPT) as well as innovative characterization technologies (IT). By fielding ITs at actual sites, nontechnical as well as technical barriers can be simultaneously identified. Of prime importance is an opportunity to involve regulators in the evaluation and fielding of these technologies as well as the ESC method itself. Side-by-side comparison of ITs with SOPT technologies, documented standard operating procedures, and confirmatory off-site analysis are some of the criteria for encouraging regulatory acceptance of ESC and any ITs.

TECHNOLOGY DESCRIPTION

This project promotes the adoption of ESC and its associated technologies, so that the costs and time associated with the U.S. Department of Energy's (DOE) site characterization program can be dramatically reduced.

The ESC methodology incorporates on-site decision-making technologies that permit site characterizations to be completed in one continuous phase. It has demonstrated that the characterization phase can be streamlined, without compromising data quality. Using both on-site analytical and multiple hydrogeologic technologies, the need to send nearly all samples off-site and the need to perform massive subsurface sampling in the absence of local hydrogeologic information is removed. By providing on-site decision-making capability, ESC can significantly reduce the probability of having to return to the site to fill data gaps. As a result, the current multiphase time sequence of data acquisition - consisting of sampling, analyzing, planning and sampling and so forth, that typically takes years - becomes compressed into a single real-time phase, requiring only months to complete. Because each new piece of information is dictated by analysis of all past data, its information content is maximized. The result is not only quicker but better site characterizations.

BENEFITS

The benefits of this project can be divided into two categories: the ESC methodology development and the demonstration of the innovative ESC analytical and geotechnical technologies. ESC has already demonstrated at two sites in FY94, the importance of early and continuous involvement of the regulators, and the utility of an on-site mobile command center to enhance the ESC process.

In FY95, at the D-Area Oil Seepage Basin (DOSB) site in Savannah River it was shown that a different management strategy can be used to execute ESC. Instead of permanent project personnel as the source of ESC management staff, task management responsibilities (e.g., analytical, geophysical, regulatory documentation, and field services) were out-sourced to both private sector consultants and components of the DOE site management team in a manner consistent with the principles of ESC and the standard operating procedures of the environmental services marketplace. Ames ESC project personnel maintained the responsibility of overall program and project management. The benefits consisted of improved ability to transfer this methodology to the private sector, and proactive involvement of the environmental remediation site team. This management mode makes the ESC methodology easier to bring to other DOE entities. As support for this contention we note that DOE at SRS has committed to performing all characterizations using ESC methodology with the Ames ESC as consultants to their EM-40 site managers starting February 1996.

COLLABORATION/TECHNOLOGY TRANSFER

The adoption of ESC and its technologies requires not only field demonstrations, but widespread dissemination of the ESC story. In FY94 and FY95, conducted tours for stakeholders at the selected sites served as the vehicle for ESC promotion.

These tours were vital in transferring an understanding of the ESC methodology, but they were nonetheless limited to those stakeholders who are able to attend (500 thus far, for three demonstrations). To build the "critical mass" of those who are aware of and understand the ESC methodology and are able to effect its adoption, the production of a variety of ESC high-impact information packages targeting environmental contractors, site managers, technology providers and regulatory communities were accomplished in FY95.

The ESC commercialization plan for these ESC information products has been implemented, including a large world wide web site that has been constructed at: <http://www.etd.ameslab.gov/technologies/projects/esc/index.html>.

ACCOMPLISHMENTS

- ESC has been accepted by DOE EM-40 for adoption at all sites at SRS, and the Ames ESC team has been contracted to provide guidance on ESC principles and practices.
- DOSB on the SRS.
- Site Specific Contaminants (SSCs) were determined during the first Phase in June, along with ground penetrating radar (GPR) and EM geophysical measurements. Innovative groundwater sampling using Geoprobe samplers without filtering was tested and confirmed to yield representative samples.

- U.S. EPA methods using gas chromatography (GC), inductively-coupled plasma (ICP) and Graphite Furnace Atomic Absorption (GFAA)-based instrumentation, plus direct push probes were fielded during the second phase held during August/September 1995 at DOSB. Eight SSC plumes were tracked in groundwater and data for baseline risk assessments and feasibility studies were obtained.
- There was acceptance of ESC at the DOSB site at SRS from the regulators from U.S. EPA Region IV and South Carolina Department of Health and Environmental Control, in particular the practice of early, proactive regulator involvement.
- Over 180 stakeholders participated in the stakeholder program at SRS DOSB site that included ESC presentations, panel discussions, technical overviews and exhibits, and on-site tours for a closeup view of the technologies in action.
- An ESC demonstration at an oil refinery in Czechowice, Poland is being planned for spring of 1996 as part of a joint DOE/Polish project.
- Nearly all ESC technologies for each of the four demonstrations were contracted from an international suite of private sector vendors, with some participation from university and DOE entities.

TTP INFORMATION

Integration of Innovative Expedited Site Characterization Techniques technology development activities are funded under the following technical task plan (TTP):

TTP No. CH13C221 "Integration of Innovative Expedited Site Characterization Techniques"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

None available at this time.

1.2

CONE PENETROMETER SUPPORT: OPERATION, MAINTENANCE, AND R&D ACTIVITY CONDUCTED ON THE OTD CONE PENETROMETER VEHICLE

TECHNOLOGY NEED

The DOE is seeking new technologies to assist in its efforts to characterize and remediate hazardous waste sites under its control. The DOE's goal is to use technologies that will reduce costs and improve the quality and timeliness of both site characterization and remediation. To help meet this goal, DOE has purchased a cone penetrometer truck that will conduct research and investigations at various sites throughout the country. This system is referred to as a Site Characterization and Analysis Penetrometer System (SCAPS).

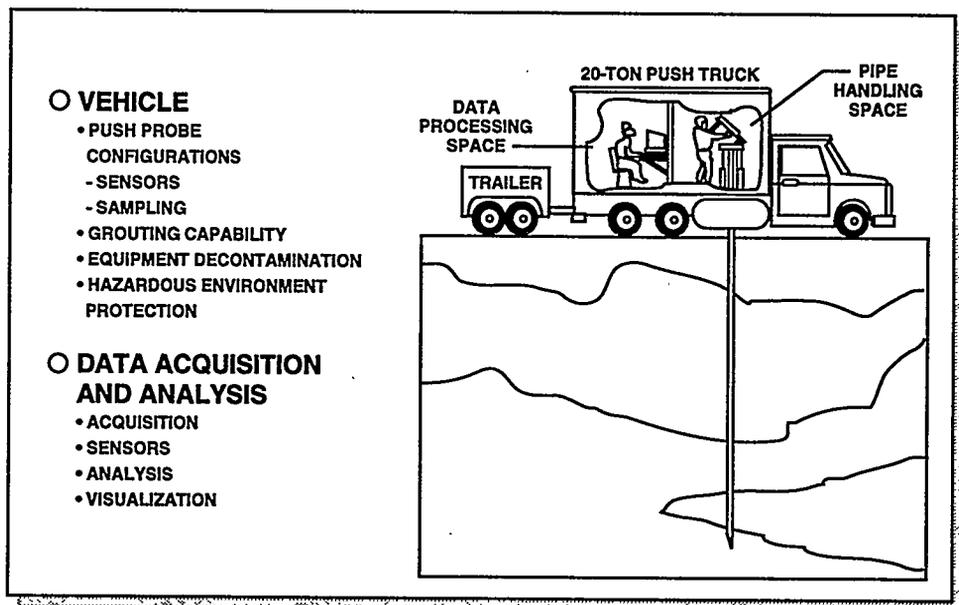


Figure 1.2-1 Site Characterization and Analysis Penetrometer System (SCAPS) Description.

TECHNOLOGY DESCRIPTION

The cone penetrometer has proven to be a safe, accurate, rapid, and cost-effective means for obtaining both subsurface samples and sensor readings of physical, geochemical, and geophysical information. The technology used in the cone penetrometer, namely hydraulic advancement of small-diameter rods, is significantly less invasive than drilling technology. It is also much safer to operate because no waste cuttings are brought to the surface. The cone penetrometer measures various parameters continuously and provides numeric measurements of material properties over the entire depth of the test. The cone penetrometer has been used effectively to retrieve

soil, groundwater, and soil gas samples. Its use in the environmental field is still in the developmental stage, but the technology has great future potential for obtaining a variety of subsurface data without bringing potentially contaminated subsurface materials to the surface.

The DOE and other government and private organizations have invested in technologies to expand the capabilities of the cone penetrometer for environmental investigations. Argonne has extensive experience in the use of the cone penetrometer, as well as in the use of a wide variety of drilling and sample collection techniques for site characterization. This experience is being used to support the field testing and evaluation of sensors and samplers for the cone penetrometer to ensure that the test environments and data interpretations are correct.

The ultimate goal of this project is to develop technologies that will broaden the capabilities of the cone penetrometer for environmental investigation and monitoring. Intermediate goals are (1) to evaluate potential new sensor, sampler, and analytical technologies in combination with the development of the necessary computer interfaces; (2) to select appropriate field sites in coordination with the Westinghouse Savannah River Company (WSRC), and to plan and execute field trials and evaluations of the new technologies; and (3) to communicate the results of the evaluations to the public and private sectors.

BENEFITS

This technology, when used in conjunction with site geological and hydrogeological controls, will enhance the integrated approach to site characterization, which is applicable at many DOE hazardous waste sites. Use of the cone penetrometer reduces the potential for exposure of site exploration personnel to hazardous materials because no wastes are brought to the surface. This approach also significantly reduces the volume of hazardous material that must be controlled and discarded as a result of the characterization. Similar benefits are realized when the cone penetrometer is used to place sampling devices in the subsurface for site monitoring.

This technology will increase versatility in sampler and sensor techniques, including borehole geophysics. Improved interactive computer software systems for real-time data acquisition and analysis will allow rapid on-site decision making.

COLLABORATION/TECHNOLOGY TRANSFER

At the beginning of FY96, a permanent base of operations was established for the SCAPS at SRS. Argonne is working with WSRC to select sites that provide the specific characteristics and contaminants needed to evaluate the new technologies. In addition, Argonne is working with the developers of these new technologies to establish the criteria for evaluation of their technologies, and to design the necessary interfaces with the SCAPS. Applied Research

Associates, Inc. (ARA) is the operations and maintenance contractor for the SCAPS.

With the completion of the demonstration phase of the SCAPS, Argonne has begun technical evaluations of sensors, samplers, and in situ analysis methods that can be adapted to the SCAPS. This phase will examine emerging and existing technologies that may be adapted to cone penetrometer technology. Results of these evaluations will be disseminated through published reports and presentations at DOE-sponsored meetings.

ACCOMPLISHMENTS

- Completed demonstration phase of the program. Using a variety of tools and techniques, demonstrations were conducted at Fernald Environmental Management Project; Pantex Site; the Portsmouth Gaseous Diffusion Plant; Dover Air Force Base; Beckley, West Virginia for the National Mine Health and Safety Academy; and Savannah River Site.
- Field trial of the position locator device (POLO), developed by UTD Incorporated.
- Field trials of three soil moisture probes, including two probes developed by ARA and Geomet, that use frequency domain reflectometry, and the time domain reflectometry probe (TDR) developed by Robert Knowlton at Sandia National Laboratories.
- Evaluation of two devices for the detection of petroleum, oils, and lubricants: the laser-induced fluorescence detector (LIF), developed by the U.S. Army Corps of Engineers Waterways Experiment Station; and the fuel fluorescence detector (FFD), developed by ARA.

TTP INFORMATION

Operation, Maintenance, and R&D Activity Conducted on the Cone Penetrometer Vehicle (SCAPS) technology development activities are funded under the following technical task plan (TTP):

TTP No CH23C222 "Penetrometer Support: Operation, Maintenance, and R&D Activity Conducted on the OTD Cone Penetrometer Vehicle (SCAPS)"

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None available at this time.

1.3

IN SITU MEASUREMENT OF VOLATILE AND SEMI-VOLATILE ORGANIC COMPOUNDS IN THE SUBSURFACE

TECHNOLOGY NEED

The projected costs for hazardous waste site assessment and cleanup in the United States are staggering. Environmental contaminants on DOE sites include radionuclides, toxic heavy metals (e.g., mercury), VOCs, semi-volatile organic compounds (SVOCs), and extractants such as tributylphosphate. Decisions concerning remediation require reliable information about the presence and extent of contamination at the facilities. The most cost-efficient means of obtaining this information is the use of minimally intrusive sampling techniques and on-site analysis (field analysis of samples). Cone penetrometer truck (CPTs) and in situ groundwater sampler provides a minimally intrusive, efficient, and cost-effective method of obtaining subsurface materials for analysis of contaminants. On-site analysis of samples has been shown to facilitate the characterization of sites by making real-time, interactive sampling decisions possible. Sampling techniques for VOCs in subsurface materials have been reported. These methods, although currently accepted, are cumbersome even when they are applied during on-site analyses. Consequently, there is a need to provide on-line, near real-time methods of analyses for VOCs and SVOCs in subsurface materials that maintain sample integrity and improve the accuracy of the analytical results by eliminating the manipulation of samples during collection, transportation, and storage.

TECHNOLOGY DESCRIPTION

The overall goal of this investigation is to develop methods and technology that will couple a CPT with field-deployable gas chromatography/mass spectrometry (GC/MS) instrumentation to transfer VOCs and SVOCs from subsurface material at depth to the analytical instrument in the field. Sampling, preconcentration, and analytical equipment will be directly coupled to a CPT to provide on-line, near-real-time analyses for VOCs (e.g., trichloroethylene, benzene) and SVOCs (e.g., polynuclear aromatic hydrocarbons, polychlorinated biphenyls) in subsurface materials. Preconcentration devices will be interfaced to GC/MS instrumentation and coupled to sampling devices housed in a CPT for in situ quantitative measurement of VOCs in soil gas and groundwater, and for screening of VOC and SVOC levels in the soil external to the penetrometer wall. The VOCs and SVOCs liberated from subsurface material will be carried to the surface by an inert, heated transfer line, preconcentrated, and analyzed by thermal desorption GC/MS.

BENEFITS

Real-time characterization of VOCs and SVOCs, in conjunction with the CPT, will dramatically improve the capabilities for Expedited Site Characterization. Time savings of real-time, depth-discrete analysis will yield rapid on-site decision-making and reduce the time required to characterize a site.

The in situ extraction of the VOCs and SVOCs reduces waste, not only in the generation of samples, which must ultimately be disposed of under applicable hazardous and/or radioactive waste disposal rules, but also in the elimination of the secondary waste generated in the laboratory with solvent extraction, column cleanup, etc.

Extensive cost savings should be realized with this approach. Substantial indirect cost savings will be realized by the rapid turn-around time of the information to those making site characterization decisions. In addition, there are quantifiable direct cost savings relative to the fixed-based laboratory analytical costs. A cost reduction exceeding 90 percent has been estimated for use of field analysis for organic characterization. Specifically, laboratory analyses using SW-846 cost \$600 per sample, while field analysis can be accomplished for as little as \$60 per sample, depending on the sample production per day. Based on DOE's estimate of 800,000 hazardous constituent analyses per year by 1994 and a typical cost of \$600 per sample, DOE will be spending about \$480 million per year for organics characterization or, over the stated life of the 30-year program, a total of \$14.4 billion. If thermal desorption GC/MS can trim 90 percent from the per-sample cost for only 20 percent of the total samples, a conservative estimate of the savings is \$87 million per year for an aggregate savings of \$2.6 billion.

COLLABORATION/TECHNOLOGY TRANSFER

Tufts University is a key technical partner on this project. As part of the effort to make information about this technology and these results widely available to DOE site users, a follow-on demonstration of the technology at a contaminated site is planned. Commercialization plans will be developed with the commercial vendor to incorporate hardware and software changes into the instrument to make the methods available to users as catalog items and to market the whole package for use at DOE sites.

ACCOMPLISHMENTS

- Established research partners through a subcontract to Tufts University
- Designed, built, and tested a laboratory prototype purge device and thermal extractor
- Evaluated transfer line materials
- Designed and fabricated transfer line
- Designed and built a prototype penetrometer purge device and thermal extractor
- Designed sampling fixture to laboratory test and evaluate analytical performance of the penetrometer purge device
- Laboratory tested the thermal extractor cone penetrometer
- Field tested the penetrometer purge device with the cone penetrometer truck

TTP INFORMATION

In Situ Measurement of Volatile and Semi-Volatile Organic Compounds in the Subsurface activities are funded under the following technical task plan (TTP):

TTP No. CH24C222 "In Situ Measurement of Volatile and Semi-Volatile Organic Compounds in the Subsurface: Development of Screening and Quantitative Field Methods Coupled to the Cone Penetrometer"

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1.4

FLOWPROBE™ CHEMICAL ANALYZER

TECHNOLOGY NEED

Conventional methods for characterizing hazardous waste sites include field sampling and transportation to laboratories off-site for analysis. This type of analysis is inherently expensive and prone to errors due to the many steps involved. The high costs of laboratory analysis is often viewed as the limiting factor for site characterization. Furthermore, slow laboratory turn-around time can result in operational delays and over treatment of sites. The validity of laboratory results is often questioned due to the loss of volatile constituents during sampling and transportation. It is viewed by some environmental personnel working in the field that at least 70% of samples that are sent to off-site laboratories are useless due to these compromises. Therefore, a need exists for quick, easy, and inexpensive methods for conducting field analysis at hazardous waste sites.

TECHNOLOGY DESCRIPTION

The FlowProbe™ Chemical Analyzer is a small, portable, chemical analyzer that measures chemicals in both liquid and gaseous states. This technology can be used wherever reagent-based chemistry exists that provides analyte concentration information detectable by optical absorption spectroscopy. The FlowProbe™ Chemical Analyzer was designed to be an in situ generic platform for performing wet chemistry-based analyses in field survey, process control, and monitoring applications. It has been packaged both as a bench-top instrument and a down-hole unit. Both configurations can perform up to 500 analyses before the reagent must be replenished. Initially there were two classes of compounds that the FlowProbe™ Chemical Analyzer was targeting: metals and chlorinated organic compounds. All chemistries and sensor materials are compatible with the measurement of analytes in aqueous matrices.

BENEFITS

The result of this project will be a commercially available FlowProbe™ Chemical Analyzer instrument that will be used to detect a wide variety of chemical species. Though sophisticated algorithms will be used to extract useful information from the reagent chemistry that is occurring, the complexity of the system will be masked. This will allow minimal required training of a field operator. The instruments have been taken to the field and fit into a standardized suitcase. The probe tip is constructed out of 316 stainless steel, allowing a variety of field uses.

Applications for this instrument include:

- Rapid site surveys—since the instrument will provide in situ analysis, the field operator can make accurate decisions on where to survey next (this information aids in mapping plume dynamics that can be used to determine feasible and requisite remediation technology).
- Stand alone, long-term, and continuous monitoring/characterization of environmental remediation and restoration sites—an operator can place the instrument in the ground and return weeks or months later to review the results instead of having to return to the site each time a data reading is required.
- In situ monitoring field applications—the ability to monitor samples in the liquid phase, downhole, provides a more representative measurement of analyte concentration (when samples are sent off site for analysis, volatilization of analytes is a concern).

COLLABORATION/TECHNOLOGY TRANSFER

Technology transfer to commercial analytical instrument manufacturers is an integral part of this project. Regular contact with personnel associated with the Center for Process Analytical Chemistry (CPAC) at the University of Washington is instrumental in allowing transfer opportunities to occur. The project is a 50/50 collaboration with CPAC at the University of Washington. The wet chemistry and casting and testing of membrane assemblies is addressed by the CPAC scientists. Engineering of a fieldable instrument is addressed by SNL. The project consists of three phases: the initial phase includes obtaining performance requirements from the various CPAC sponsor chemical companies (i.e., users) and working with the CPAC instrument companies (i.e., suppliers) early in the development of the instrument. The second phase is to demonstrate the instrument in the field at DOE and commercial sites. The final project phase is, in collaboration with an instrument manufacturing partner, to make a pre-commercial prototype. LifeSciences of St. Petersburg, FL, signed a commercialization agreement on February 12, 1996. A first generation prototype based on the SNL design is being brought to market in late summer 1996. Letters of interest from other CPAC companies, including in-kind support commitments that range from \$200K (Dow USA) to \$50K (Perkin-Elmer Corporation) have been received. Other companies expressing interest and in-kind support commitments include: Amoco, Calgon, Chevron, Sippican, Goodyear, Hewlett-Packard, Proctor & Gamble; Shell, and ZymoGenetics.

ACCOMPLISHMENTS

Since the project started in November 1993, the following has been accomplished:

- Industry has been solicited for input on instrument usage and design requirements.

Responses were obtained from 25 different potential commercial users and instrument manufacturers. Based on the industry identified requirements, we partitioned the functions of the instrument into seven subsystems: six hardware-related and one chemistry-related.

- SNL led a conceptual design review in which representatives from CPAC sponsor companies and personnel from Los Alamos National Laboratory (LANL) and SNL worked together to define the operational needs for the FlowProbe™ system model. Subsequent to this meeting and after design of a prototype, SNL organized a prototype design review with CPAC industry sponsor representatives and scientists from LANL and SNL to review the technical status of the project.
- SNL designed and built test pieces of subsystem assemblies as individual units.
- Multiple probe heads were assembled for testing the subsystems as complete units.
- Various polymer membranes were cast and examined using the probe heads for chemical compatibility and analyte partitioning into the reaction cell.
- Four different field tests were performed:
 - W.R. Grace, monitoring water in a pilot plant for boiler water. Established 250 ppb detection limit with 80% precision.
 - Dow Corning, monitoring Cu in silane processing stream. Ran on-line one week unattended with a 250 ppb detection limit.
 - Martin Marietta Specialty Components Division, monitoring of chlorinated organics was attempted at a remediation site. Due to external forces, the instrument did not go on line.
 - Dow Chemical, tested bench top in lab. Standard addition of analytes in water was successful, but had matrix problem of actual process line chemicals. Test was inconclusive.
- Probe assemblies were delivered to Boeing and LANL for testing and evaluation.
- Down-hole, or submarine unit, has been built and lab tested.

- Active in commercialization activities with LifeSciences, St. Petersburg, FL.

TTP INFORMATION

FlowProbe™ Chemical Analyzer technology development activities are funded under the following technical task plan (TTP):

TTP No. AL24C222 "FlowProbe™ Chemical Analyzer"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

None available at this time.

1.5

PORTABLE ACOUSTIC WAVE SENSOR SYSTEMS FOR VOLATILE ORGANIC COMPOUNDS

TECHNOLOGY NEED

Many DOE sites have been contaminated with VOCs, such as carbon tetrachloride at the Hanford Site, and trichloroethylene (TCE) found at the Savannah River Site. In addition, there are a large number of non-DOE sites that have also been contaminated with VOCs. To characterize this contamination, sensors are needed that can provide rapid field screening before, during, and after remediation processes. Systems are also needed for real time, on-line monitoring of contamination levels in process streams during the remediation. For example, monitoring of VOCs in off-gas streams during soil vapor extraction operations can help to document the effectiveness of the remediation and to optimize its performance. Finally, sensors that can be used for in situ monitoring can alleviate the many sampling problems that arise, especially with deep monitoring wells.

TECHNOLOGY DESCRIPTION

The portable acoustic wave sensor (PAWS) technology consists of one or more surface acoustic wave (SAW) sensors utilizing sorbent coatings to detect chlorinated hydrocarbons (CHCs) and other VOCs as shown in Figure 1.5-1. By measuring the velocity and attenuation of the sensor(s) as chemical species are sorbed into the coating(s), rapid and sensitive detection can be achieved. As described in more detail below, this project is being performed in collaboration with three U.S. companies: Sawtek, Inc.; General Atomics; and, Nomadics, Inc.; as well as with Pacific Northwest National Laboratory (PNNL). This collaborative project involves designing, developing, and field-demonstrating a versatile hand-held monitoring instrument of environmental and occupational safety interest, for VOCs, including the CHCs of particular interest to DOE. These instruments will include an array of coated SAW sensors, environmental sampling and pretreatment systems, analog and digital electronics, microprocessors, and data analysis software. The systems will be designed to provide rapid, real-time monitoring of one or more VOCs with detection levels at or below regulatory levels. Species identification will be performed using pattern recognition techniques on the multiple responses from the sensor array. For more information on SAW sensor arrays and pattern recognition techniques, see the companion report in this volume on "Surface Acoustic Wave Array Detectors".

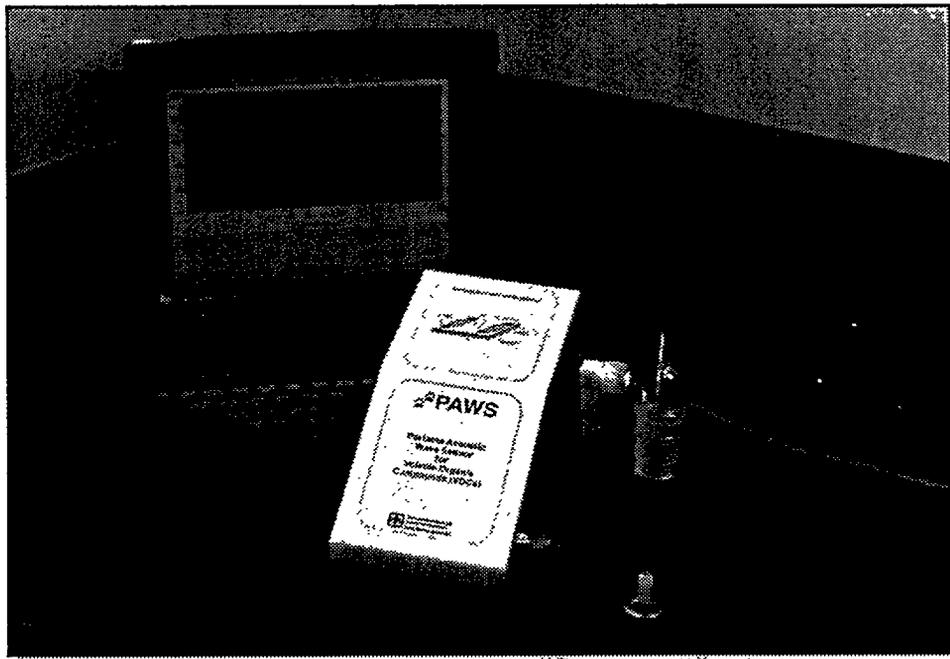


Figure 1.5-1 Schematic of a surface acoustic wave sensor with an on-chip temperature probe (RTD) for temperature control and compensation.

Current project activities are focused in three main areas. The first task involves developing and demonstrating environmental sampling systems using preconcentrators and semi-permeable membranes that will increase the versatility and ruggedness of the PAWS technology. Sensing capabilities are being extended to provide lower detection levels (about a factor of 100 lower), an improved resistance to interfering chemicals, and an ability to provide rapid, field analysis of water samples. Issues such as chemical compatibility, speed of analysis, and power requirements are being considered in this development.

The second task involves developing and fabricating an initial SAW array prototype system to be field tested this year to demonstrate capabilities and provide insight into key areas for improvement. This work involves various hardware components including analog drive electronics and multiplexers for the SAW array; data acquisition and control electronics; relays for activating pneumatic components; and batteries, power supplies and converters. In addition, software is being developed to operate the system, take the relevant SAW array responses, and present the results.

The final task involves providing technical assistance and advice to various project collaborators based on our extensive experience in developing, fabricating, and field testing environmental monitoring systems based on SAW sensors. Part of this work involves limited testing of coated SAW sensors to validate and expand on the main characterization effort at PNNL.

BENEFITS

PAWS can perform continuous, on-line or in situ, monitoring with rapid and reversible response. In comparison to off-site analysis of grab samples, PAWS performs real-time monitoring, a key benefit when conducting remediation activities. The systems are small, portable, and easy to set up and use. Combined with the low system cost, the low operating costs make the PAWS technology much less expensive. The sensor can be configured so that it can be placed downhole for in situ monitoring and can be automated to provide chemical information to site remediation workers. Current PAWS systems have capabilities for determining molecular species and concentrations of isolated chemicals. Systems under development by this collaborative team will be able to analyze multiple species in mixtures in either air or water. Detection levels will be at or below typical regulatory action levels. PAWS is fast, cheap, and as safe as currently available alternatives, such as gas chromatographs or infrared analyzers.

COLLABORATION/TECHNOLOGY TRANSFER

This project is being performed in collaboration with three U.S. companies and PNNL. The companies are providing significant development resources and will be the avenue for commercializing the technology. This collaborative program was established based on a Commercialization Plan executed by the Principal Investigator (PI). The names and roles of the various industrial parties are: (1) Sawtek, Inc., a leading supplier of SAW devices, is developing and will be a commercial supplier of the SAW array assembly, including the SAW sensors with appropriate polymer coatings, a test fixture with gas sampling ports, temperature control and compensation circuitry, and SAW drive electronics, (2) General Atomics is responsible for networking hardware for application of these systems at environmental sites, and (3) Nomadics, Inc. is designing and developing PCMCIA-based data acquisition and control electronics compatible with the SAW array systems being developed, along with Windows-based software for system control and data acquisition and analysis. The role of PNNL is described in a separate report in this volume, titled "Surface Acoustic Wave Array Detectors." As a result of this collaborative team effort, a SAW array system for VOCs should be commercially available in 1997.

ACCOMPLISHMENTS

- A small PAWS module as shown in figure 1.5-2 with an adsorbent preconcentrator was fabricated and interfaced with a PCMCIA data acquisition and control card from Nomadics, Inc. Laboratory tests demonstrated quantitative analysis of trichloroethylene (TCE) in air from less than 100 ppb to over 200 ppm. In conjunction with Nomadics, this system was demonstrated at Tinker Air Force Base for detection of TCE in air in process

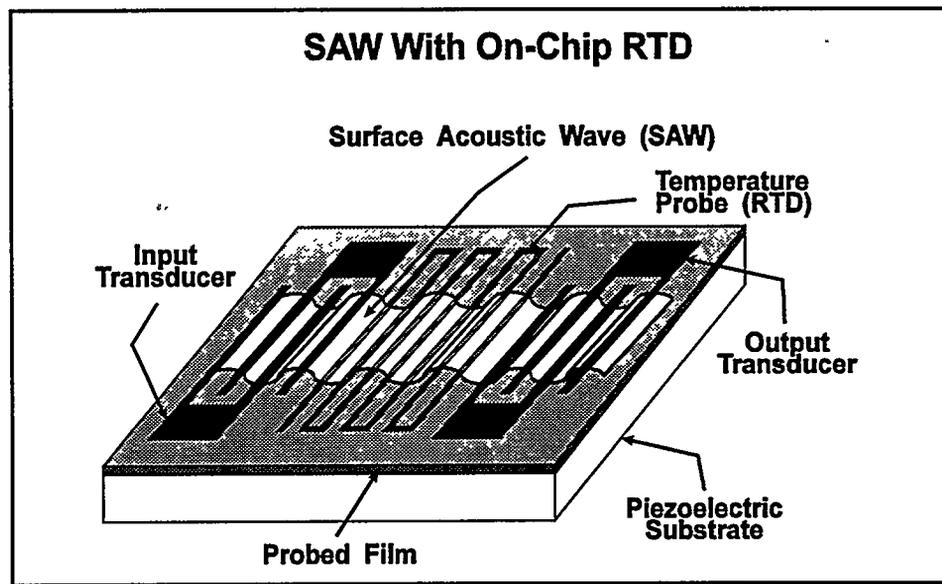


Figure 1.5-2 Picture of a small single SAW sensor module with an adsorbent preconcentrator for trace detection of isolated VOCs in air and water.

streams at a water treatment facility. Water analysis capabilities were also demonstrated.

- Using adsorbent preconcentrators, detection of key VOCs in air was demonstrated at levels below 100 ppb. Detection of sub-ppm levels of TCE and carbon tetrachloride in corrosive streams containing up to 4000 ppm of Hydrochloric Acid vapor (relevant for monitoring exhaust from on-site destruction systems for CHCs) was also demonstrated. A variety of adsorbents have been evaluated for key VOCs to optimize selection for specific applications.
- Demonstrated water analysis using purge-and-trap type systems with current detection limits for typical VOCs down to the 5-50 ppb range as shown in Figure 1.5-3.
- Components for the SAW array system have been developed, including a small (58mm on a side), low power (30 mA) data acquisition and control card with full capabilities, software for operating this card to control the system and to acquire SAW response data, and a relay card for actuation of pneumatic components. A miniaturized version of a patent pending SAW drive circuit is being fabricated along with multiplexers for operating up to eight SAW sensors.
- A bench-top PAWS system using a single SAW sensor was developed for real-time, on-line monitoring of isolated VOCs. This system was demonstrated at both Hanford and Savannah River for monitoring of VOCs in off-gas streams, from soil vapor extractions systems, and samples pulled to the surface from a cone penetrometer probe. The system was shown to be easy to set up and use, and demonstrated its ability to provide rapid and accurate analysis.

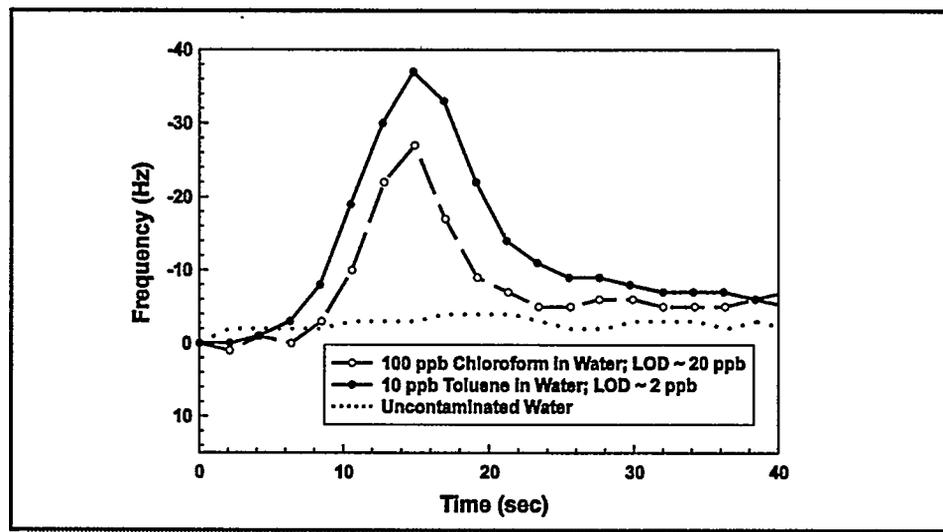


Figure 1.5-3 Response of poly(isobutylene)-coated SAW device during thermal desorption of an adsorbent preconcentrator loaded by purging water samples for one minute (total cycle time three minutes). The small response to no water, compared with the responses with trace amounts of VOCs, demonstrates the current capabilities for water analysis.

- A downhole PAWS system (single SAW sensor) with associated packers was developed for in situ monitoring of isolated VOCs in vadose zone boreholes, with diameters over 4 inches. This downhole probe was demonstrated at Hanford, providing continuous in situ monitoring of carbon tetrachloride concentrations from 10 to over 20,000 ppm.

TTP INFORMATION

Portable Acoustic Wave Sensor Systems for Volatile Organic Compounds technology development activities are funded under the following technical task plan (TTP):

TTP No. AL22C221 "Portable Acoustic Wave Sensor Systems for Volatile Organic Compounds"

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1.6

SURFACE ACOUSTIC WAVE ARRAY DETECTORS

TECHNOLOGY NEED

Characterization, monitoring, and cleanup of contaminated DOE sites will require field deployable analytical techniques such as chemical sensors. Chlorinated hydrocarbons contaminate soil and groundwater at over ten DOE sites. At each individual site, concentrations found vary widely. Sensors used at these sites must be sensitive and selective, operate over a wide dynamic range, and suitable for deployment in field environments.

TECHNOLOGY DESCRIPTION

The purpose of this task is to design, develop, and demonstrate array sensor systems for sensing volatile organic compounds (VOCs), including chlorinated hydrocarbons and other vapors of interest, to environmental cleanup and occupational safety. These sensor arrays are based on polymer-coated SAW vapor sensors and data processing, using pattern recognition and chemometric techniques. Key elements of this effort include the rational choice of polymer materials for use as the selective sensing layers; a predictive method for sensor performance; experimental evaluation of sensor arrays for VOC detection; and pattern recognition and other chemometric techniques for converting data into chemical information.

The advantages of the SAW vapor sensor technology include the rugged planar design of the devices; the suitability of polymer-coated devices for use in arrays with pattern recognition; fast response times (seconds); rapidly reversible responses (the selective material is not altered by the vapor); high vapor sensitivities (ppm to ppb detection limits depending on the particular vapor); and the flexibility of the array approach to be adapted to many detection problems. The analyte(s) to be detected by a SAW sensor array system can be changed merely by the selection of the polymer coatings and the pattern recognition algorithm used.

The sensor array approach provides greatly increased selectivity and reliability in field environments over a single sensor. Single sensors cannot determine if an interfering species is present that might invalidate the measurement. In addition, sensor arrays offer the possibility of detecting and quantifying multiple analytes with the same system. The compact SAW sensor array systems envisioned will convert data into chemical information and communicate it in a form necessary for decision making. Thus, SAW sensor technology will become the basis for practical, fieldable solutions to characterization and monitoring problems.

This task is part of a collaborative effort in the development of SAW array systems. The team includes two National Laboratories and a number of commercial partners (see below). The task at PNNL is focused specifically on the scientific and technical aspects of selecting and using polymers as the sorbent layers on SAW sensors for sensor arrays.

BENEFITS

Appropriate sensing of VOCs during environmental cleanup will improve worker safety; aid in decision making on types of protective equipment required and length of time workers can stay in the environment; and reduce costs by measuring multiple vapors with a single instrument rather than requiring separate sensors for each vapor.

COLLABORATION/TECHNOLOGY TRANSFER

This work is being coordinated with SAW sensor development tasks at SNL. We have a funded collaboration with Sawtek, Inc, and General Atomics for the development and commercialization of SAW sensor array instruments.

ACCOMPLISHMENTS

This task began with a modeling effort to develop a rational approach for the selection of polymeric sensor coating materials for SAW sensor arrays. This approach was based on using linear solvation energy relationships (LSERs) to model the sorption of vapors by polymers and predict polymer/gas partition coefficients. Using models for SAW sensor transduction mechanisms, these partition coefficients were converted to sensor responses. These models were validated against experimental sensor response data. Polymers offering optimal sensitivity for various classes of vapors were identified. Predicted limits of detection were compared with permissible exposure limits and threshold limit values. It was found that SAW vapor sensors could detect the majority of vapors considered at regulatory levels.

In addition, the modeling effort was used to compare the performance and selectivity of polymer materials with other novel materials appearing in the literature. It was found that assembled fullerene materials did not offer substantially different selectivities than low polarity polymers. Similarly, it was found that cavitated-type materials purported to operate via molecular recognition did not offer different selectivity than amorphous polymers. These results indicated that our original plan to use polymers as the selective layers on our sensors was appropriate.

Polymers for SAW vapor sensors have been screened in a large experimental program testing 20 different polymer materials as sensing layers against 19 vapors, each at four concentrations. Polymer-coated sensors were examined for film morphology, speed and reversibility of sensor responses, sensitivities to vapors, and linearity of calibration curves. In addition, chemometric techniques have been used to examine relationships among the test polymers.

Chemometric methods have also been used to examine the ability of arrays of polymer-coated sensors to discriminate and classify vapors. Dendrograms showed excellent clustering of vapor data as shown in Figure 1.6-1. Chemometric models were able to classify low polarity vapors by compound class; for example, aliphatic hydrocarbons, aromatic hydrocarbons, and chlorinated hydrocarbons. In further analysis, it was found that all the chlorinated hydrocarbon vapors tested (perchloroethylene, trichloroethylene, carbon tetrachloride, and dichloromethane) could be distinguished from one another as well as from all the other vapors.

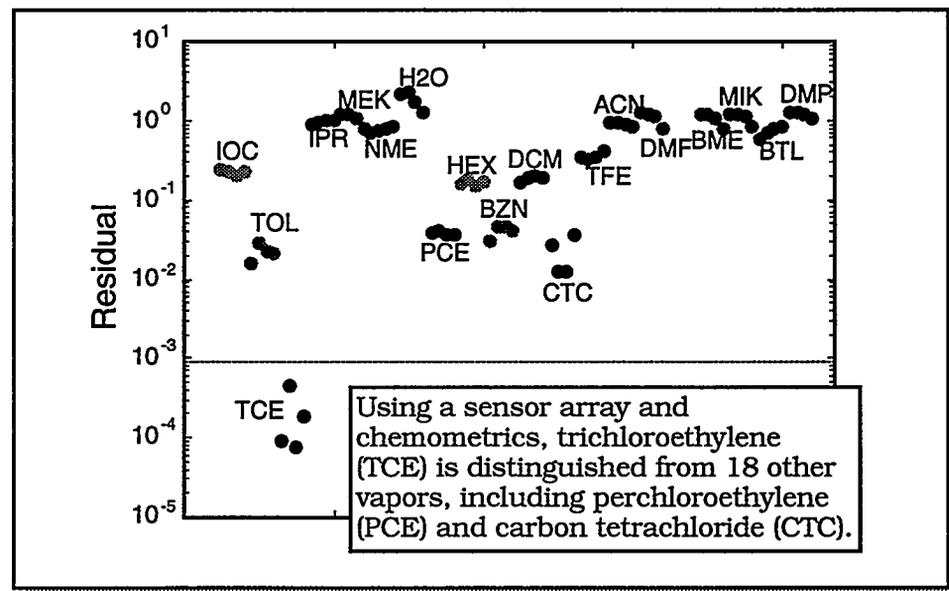


Figure 1.6-1 Results for the classification of trichloroethylene (TCE).

TTP INFORMATION

Surface Acoustic Wave Array Detectors technology development activities are funded under the following technical task plan (TTP):

TTP No. RL35C222 "Surface Acoustic Wave Array Detectors"

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None available at this time.

ANALOG SITE FOR CHARACTERIZATION OF CONTAMINANT TRANSPORT THROUGH FRACTURED ROCK

TECHNOLOGY NEED

Many contaminated sites are located in fractured rock. For example, the ORNL has significant contamination in fractured shale. INEL and the Hanford Sites have problems in fractured basalt. The characterization of these sites in order to predict the transport of contaminants can be problematic. The location of fractures is often a mystery, and their effect on flow can be dramatic. The fractures themselves may be leached by reactive waste material. Containment of the waste may require the sealing of fractures. Thus, the three key issues that influence remediation of these sites are:

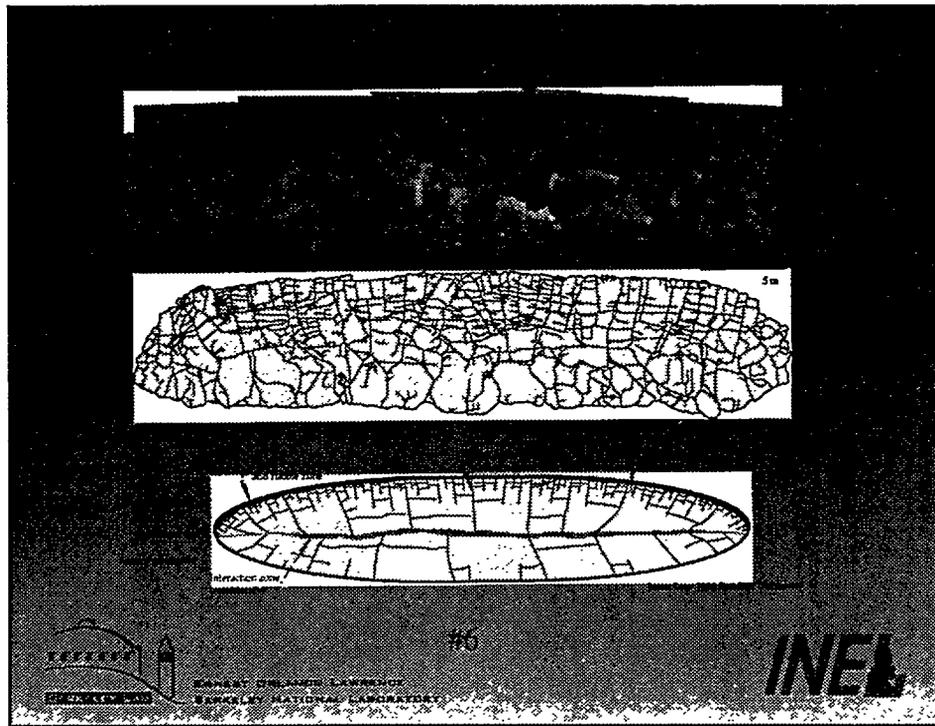
- Finding the fractures that control fluid flow and transport
- Analyzing fluid flow and transport in the fracture system
- Controlling of contaminant transport in the fracture system

TECHNOLOGY DESCRIPTION

This project is designed to identify reliable tools and methodologies for characterizing the fracture systems that control flow and transport in specific geologic settings. Characterization tools will be used to predict the outcome of flow and transport experiments in fractured rock in order to assess the utility of these tools for characterizing important hydrologic features in similar contaminated sites.

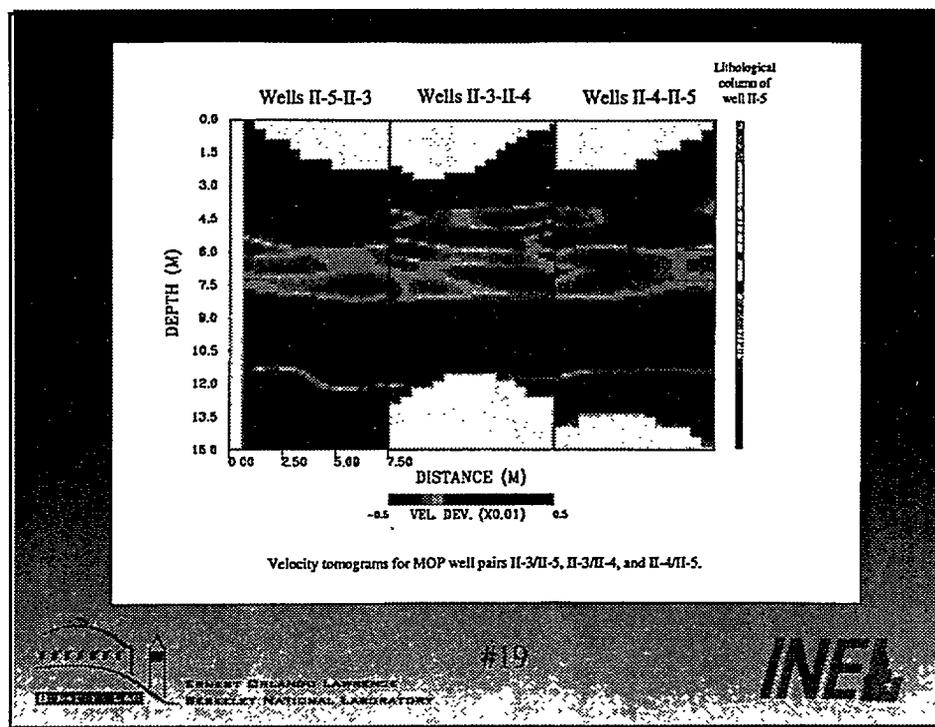
At an analog site in the Snake River Basalts, two series of measurements are being performed. The first series is designed to characterize the hydrology of the site. The second set is a flow and transport experiment designed to test the predictive capability of the characterization methodology.

The characterization phase began with a geologic investigation designed to identify the style of fracturing and the likely fracture patterns as shown in Figure 1.7-1. Then geophysical investigations were performed to locate the features of the fracture system that control fluid flow. Radar reflection and tomography, and hydraulic interference testing was used as shown in Figure 1.7-2. The interpretation(s) of these measurements will consist of one or more estimates of the location of important hydrologic fractures, and how they are connected. These features will then become part of the conceptual model for infiltration.



GFX.96-0196

Figure 1.7-1 Idealized fracture geometry in a basalt flow cross-section



GFX.96-0170

Figure 1.7-2 Velocity tomograms for MOP well pairs II-3/II-5, II-3/II-4, II-4/II-5

An infiltration test is planned for the summer of 1996. Test design and site preparation are underway as shown in Figure 1.7-3. The test will be conducted over an area less than 10m by 10m. Parallel slanted boreholes have been drilled at the site and will be instrumented to detect fluid flow. Instrument placement will be determined based on the conceptual model developed with FY95 data. Two pairs of slanted holes will be used for geophysical monitoring with radar tomography, which will be done before and during the infiltration test. The idea is to image the flow through flow-induced changes in geophysical properties. Comparison of the flow experiments with the flow patterns predicted in the first phase will provide a format for identifying those methods, or combinations of methods, that successfully identify the fractures that control flow.

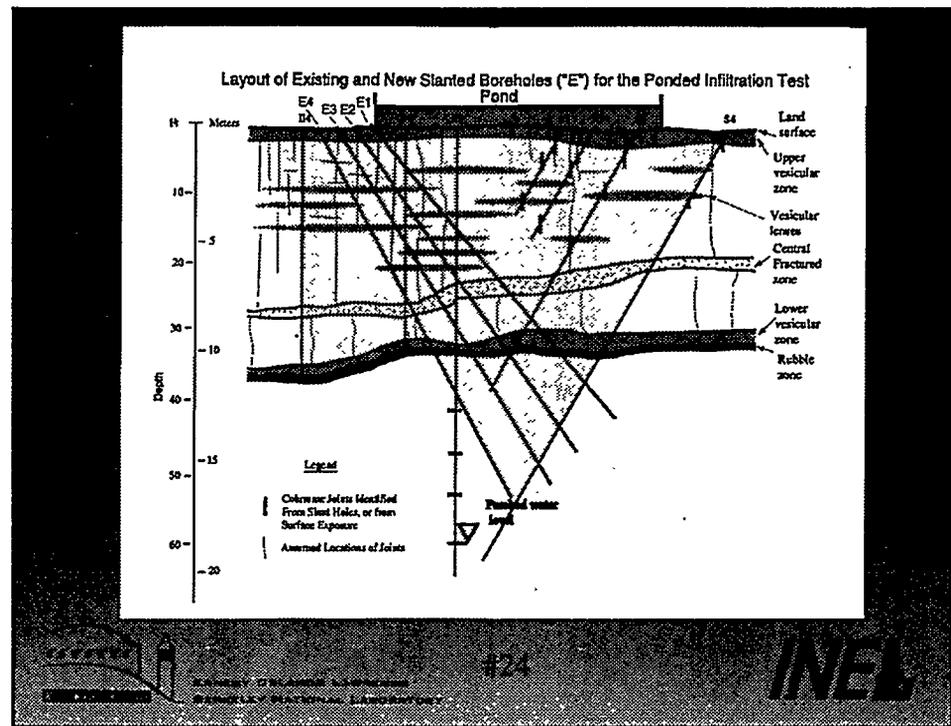


Figure 1.7-3 Layout of existing and new slanted boreholes ("E") for the ponded infiltration test

BENEFITS

The results of this project fall in two categories. First, the project is being conducted in a rock mass that is analogous to a significantly contaminated rock mass. Therefore, the tools developed and checked at this site will be reliable for use in the real contaminated site. The radar method tried at Box Canyon is applicable to characterization of the OCVZ (Organic Contaminated Vadose Zone) site at INEL. Many of the vadose zone instruments such as the deep tensiometers are of use to the ICPP or the RWMC (Radioactive Waste Management Complex). More importantly, the methodology for characterizing fractured materials at the INEL contaminated sites can be extended to other sites, making it possible to move on to new geologic settings much more efficiently.

COLLABORATION/TECHNOLOGY TRANSFER

Parsons Environmental participates in the project as a contractor. Stanford University provides the geologic investigation of fracture systematics. EMI, Inc., a small business, is contracted for geophysical surveys. Traditional geophysical service companies and other geotechnical firms can learn from this project, either by direct participation or through the results of the project. Interest in the technology developed by the project could be quite large, as there are many contaminated sites in fractured rock. In FY95 we collaborated with a DoD database design project.

ACCOMPLISHMENTS

A study site has been identified in the Snake River Basalts at the Box Canyon site, and a close collaboration between Berkeley Lab and INEL has been established. A successful field season in FY95 included hot air injection tests, air interference tests, radar tomography and geologic investigations. The hot air injection into boreholes was designed to find connections between the fractures below the ground and the surface. No temperature changes were detected at the surface, but connections were determined between boreholes. Then air interference tests were conducted to determine the connections between the fractures. Radar tomography was tested and produced high resolution images, which delineated the major features of the site quite well. Vadose zone instrumentation designed to work in fracture systems was designed and tested.

In addition, four other tasks were completed. A study was conducted to determine the feasibility of using a combination of isotope ratios and hydraulic head to determine the location of fast pathways in the Snake River Aquifer. This study had favorable results and led to a successful new proposal to do this work. A second study used hydrologic inverse methods designed specifically for fractured rock to analyze the data from the Large Scale Aquifer Stress Test. The results revealed the salient features of the heterogeneity in the fractured basalts, and indicated the utility of using this type of analysis in the basalt aquifer. A third study compared the use of the CSAMT (Controlled Source Audiofrequency Magnetotelluric) method with that of resistivity at the site of the Large Scale Infiltration Test (LSIT). The CSAMT method is a version of magnetotellurics which has advantages over simple resistivity. The two methods produced similar anomalies. Finally, we developed a database management system (AVS) that was directly linked to the application visualization system for LSIT data, allowing the user to select and immediately visualize data in one system.

TTP INFORMATION

Analog Site for Characterization of Contaminant Transport Through Fractured Rock technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. SF141001 "Analog Site for Characterization of Contaminant Transport Through Fractured Rock"

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1.8

INTERNATIONAL ENVIRONMENTAL ASSESSMENT/ JCCEM CONTAMINANT TRANSPORT STUDIES

TECHNOLOGY NEED

Validation of existing DOE contaminant transport models through exchange of contaminant-migration data and joint U.S.-Russian modeling of well characterized contaminated Former Soviet Union (FSU) sites will help site managers obtain approval from regulators for fewer samples, analyses, wells, and stronger cases for No Further Action (NFA) at many DOE sites.

TECHNOLOGY DESCRIPTION

Nuclear fuel cycle activities of the FSU have resulted in significant contamination of the environment in western Siberia. The West Siberian Basin contains the largest amounts of surface and subsurface radioactive contaminants on earth. PNNL is developing, jointly with their Russian counterparts in the Ministry of Atomic Energy of the Russian Federation (MINATOM), three-dimensional numerical models of the hydrogeology and potential contaminant migration in the West Siberian Basin to verify and validate DOE models and modeling strategies using decades of data from measured contaminant migration at the Mayak, Tomsk-7, and Krasnoyarsk-26 sites. These joint models will also be used in designing mitigation strategies for the sites. DOE uses such models to evaluate the potential for risk from contaminated U.S. sites, and will benefit both from model validation and from technologies transferred from Russian site remediation work.

The long-term goal of this work is to determine and improve the capability of DOE's contaminant transport models to predict future environmental and human impacts of radioactive contaminant releases, such as those that have occurred to date in the West Siberian Basin. Our objectives for FY95-96 are to: 1) document results of the regional hydrogeologic model of the West Siberian Basin; 2) develop and document the spatially registered, digital geologic and hydrologic databases derived from open-literature sources and direct interactions and subcontracting with MINATOM, that will provide a common database for joint U.S.-Russian modeling in geographic information system format; 3) implement the conceptual and computer models of the hydrogeology of Tomsk; and 4) perform preliminary joint U.S.-Russian hydrogeologic contaminant-transport model inter-comparison studies for Mayak.

BENEFITS

- Technical collaboration with FSU states and scientists on large-scale groundwater contaminant migration
- Validation of groundwater transport models of DOE scientists with decades of Russian groundwater sampling data

COLLABORATION/TECHNOLOGY TRANSFER

Technical expertise from the United States, including joint activities by PNNL and Savannah River Technology Center, is being brought to bear on large-scale groundwater contaminant migration.

ACCOMPLISHMENTS

- Completed the regional hydrogeologic model for the West Siberian Basin and published a definitive PNNL report and an open-literature synopsis in May 1995. This is, to our knowledge, one of the largest geographic areas ever attempted for modeling, and is the proof-of-principle for the systematic approach to remote/local site characterization and analysis that is the basis of our technology.
- Completed a joint U.S.-Russian workshop on hydrogeologic modeling of the West Siberian Basin and Mayak, Tomsk-7, and Krasnoyarsk-26 sites at PNNL in August 1995. This workshop provided Russian peer review of PNNL's site characterization and modeling efforts to date (positive feedback), and formalized plans for FY96 and outyear cooperative U.S.-Russian site, characterization database development and contaminant-transport modeling.
- Completed the remote characterizations for the Mayak and Tomsk sites and published letter reports in September 1995. These two databases form the framework for FY96 and outyear joint databases incorporating Russian site characterization data, which will be one of the principal joint U.S.-Russian project activities.
- Completed the computer implementation for the Tomsk intermediate-scale hydrogeologic model using remote characterization data. Refinement of this model in FY96 and outyears using Russian site characterization data will be one of the principal joint U.S.-Russian project activities.

TTP INFORMATION

International Environmental Assessment and the Joint Coordinating Committee on Environmental Management (JCCEM) Contaminant Transport Studies technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. RL34C221 "International Environmental Assessment"

TTP No. RL35C223 "JCCEM Contaminant Transport Studies - PNNL"

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2.0

PROJECTS FOR THE RADIOACTIVE TANK WASTE REMEDIATION FOCUS AREA

Several innovative characterization technologies are needed to solve key problem areas in the Radioactive Tank Waste Remediation Focus Area (TFA). They include: sensors integration with deployment systems for in situ determination of chemical and physical properties of tank waste; in-tank geophysical methods for imaging waste matrix characteristics; and real-time, on-line systems to monitor and control retrieval, transfer, and treatment operations. The sensor deployment systems include cone penetrometers, the Light Duty Utility Arm (LDUA), and other mechanic arm delivery systems.

Many technologies are being developed in FY96 to help address the identified problem areas. An acoustic monitoring system is being deployed on a mixer pump to determine the mixing radius and the density of mixing fluids. A miniaturized resonator system is also being developed for monitoring the density and viscosity of supernate and liquids. In the area of sensor deployment systems, a specially instrumented cone penetrometer probe is being developed for insertion into the tanks via risers. A new solicitation will be issued for technologies that can sample waste throughout the tank and not just under the risers. The electromagnetic induction system for deployment in liquid observation wells (LOWs) and the neutron activation probes for deployment in LOWs or by cone penetrometer truck (CPT) have been developed for monitoring moisture content of tank waste. Sensors previously developed for monitoring contaminant plume in the subsurface are being considered for integration with the CPT and LDUA for in-tank deployment. One notable technology is the cone penetrometer Raman probe with neural network data analysis. Several on-line sensors are under development for monitoring fluid transport properties; i.e., viscosity, density, and volume percent solids. In addition, an electric resistivity tomography technique is being developed for monitoring tank leaks during the sluicing retrieval of tank waste.

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2.1

ELECTRICAL RESISTANCE TOMOGRAPHY FOR SUBSURFACE IMAGING

TECHNOLOGY NEED

Electrical Resistance Tomography (ERT) technology can be used for detecting leaks from the Hanford single-shell tanks. DOE has approximately 149 single-shell tanks that have been used to store high-level mixed wastes, many located at the Hanford site. It is known that 60 to 70 of these tanks were leaking and releasing their contents to the surrounding soil. Other tanks may be leaking, but the existing techniques for determining leakage prevents an accurate assessment. In line with the potential for danger such releases pose to site personnel and longer-term danger to the surrounding communities, environmental regulations require that even small volume releases from these tanks be reported. There is a clear need to be able to detect when a tank begins leaking so that corrective measures can be taken before damage is great. There is also a need to be able to isolate the leak location in the event that tank repairs are practical.

There are currently two methods for detecting leaks, and neither is useful for locating the precise location point. The simplest method is a careful inventory of tank contents. Unfortunately, the precision needed in level sensing is not simple with the nasty conditions in these tanks. Even level sensors are troublesome due to the large chunks of waste in some. The other approach is to drill beneath the tank and install sensors. This method also presents problems since these sensors provide point measurements under the tank, and any leakage will be highly channeled due to the heterogeneous soil at Hanford and will likely be missed.

In situ remediation of contaminated sites requires at least two activities. First, it is necessary to characterize the relevant parameters of the site (e.g., geology, hydrology, geochemistry). Second, it is necessary to monitor whatever method is used to accomplish the remediation in order to control the process and evaluate the final results. Current technology for both tasks is often based on drilling and sampling, which is expensive, invasive, and often produces a very sparse data set. A technology is needed to provide high-resolution information between boreholes. ERT is designed to fill in this missing information. A 2.5-dimensional code has proven useful for many applications, especially for cross-borehole imaging where the subsurface is approximately two dimensional. However, much of the world cannot adequately be approximated by two dimensions. There is a clear need for accurate three-dimensional images of subsurface properties and processes. Such a capability would be very valuable in environmental restoration work, as well as many other geophysical and geotechnical areas.

Much of the subsurface soil and groundwater contamination that DOE is required to cleanup is contaminated with nonaqueous phase liquids (NAPLs). Unfortunately, most of these liquids are very difficult to detect without drilling a borehole and testing a soil or water sample. Because the subsurface is usually very heterogeneous, a lot of drilling is needed for this approach to adequately map most contaminant plumes. A method is needed to look beneath the surface, or perhaps between boreholes, and map the three-dimensional extent of NAPL contaminants. This ability would make possible estimates of the contaminant mass, lateral extent of the plume, speed and direction of transport, and would greatly aid in designing remediation strategies.

TECHNOLOGY DESCRIPTION

The goals of this task are to: (1) develop and demonstrate a system for detecting and locating leaks in the single shell tanks at the Hanford Site; (2) develop a practical, fully three-dimensional inverse code for ERT; and (3) extend research and development for detection of NAPLs by a small-scale ERT imaging experiment of a trichloroethylene (TCE) or polychloroethylene (PCE) release at the Oregon Graduate Institute (OGI) LEAP tank facility.

BENEFITS

The technique is based on the automated measurement and computerized analysis of electrical resistivity changes caused by natural or man made processes, such as surface water infiltration, underground tank leaks, and steam or electrical heating during soil cleanup.

ERT has a variety of applications:

- Site characterization in soil remediation projects
- Detection and location of subsurface leaks
- Evaluation of effectiveness of cleanup techniques
- Cleanup process control
- Nondestructive evaluation of large structures such as pavements, buildings, and dams

ERT has strong advantages over competing techniques:

- Provides unprecedented detail of subsurface structures and processes (resolution is roughly equal to electrode separation)
- Two- and three-dimensional imaging is possible
- 50% to 75% fewer boreholes are needed than in conventional borehole-sampling techniques

- Updated survey images can be available in one to six hours
- Effective at depths of 10 to 500 ft.
- Stainless steel electrodes are rugged, inexpensive, and easily emplaced
- ERT has been demonstrated in both clay-rich and sandy soils

COLLABORATION/TECHNOLOGY TRANSFER

Collaboration is ongoing with SteamTech Inc., an environmental remediation service company, to transfer the basic ERT technology. That work began in FY95 and continued into FY96. Collaboration is also ongoing with Prof. Douglas LaBrecque at the University of Arizona and with Prof. Andrew Binley at the University of Lancaster, England. Their contributions to the project are mainly computer code development. Collaboration is ongoing with Westinghouse Hanford Co. (EM-40), in the development of tank leak detection technology. Collaboration is also ongoing with Rick Johnson at the OGI in the NAPL experiment.

ACCOMPLISHMENTS

Detecting leaks from the Hanford underground, single-shell tanks is a continuing task. At the DOE Hanford Site, a storage tank test facility has been constructed that can be used to test schemes for detecting tank leaks. This facility has been used for two tests in FY94, which were designed to use electrical resistivity images under the tank to detect and locate leaks. The first test was for a 'bath-tub ring' leak where water was released from the tank along one side, and ERT images under the tank were successful in following the plume of water in the soil as a function of time and space down to a depth of 35 feet (the limit of our electrodes). The second test was for a leak from the tank bottom, where water was released from beneath the tank.

Development of a fully three-dimensional ERT code is underway. A test version of the three-dimensional inversion code has been written. It incorporates a new version of the forward solver, which is designed to be more accurate and faster than the previous solver. Initial tests were on synthetic data and some limited tests have been on field data. The performance remains very slow—inversions of typical data sets require one to three days of Central Processing Unit (CPU) time on a Sun Sparc 5 workstation.

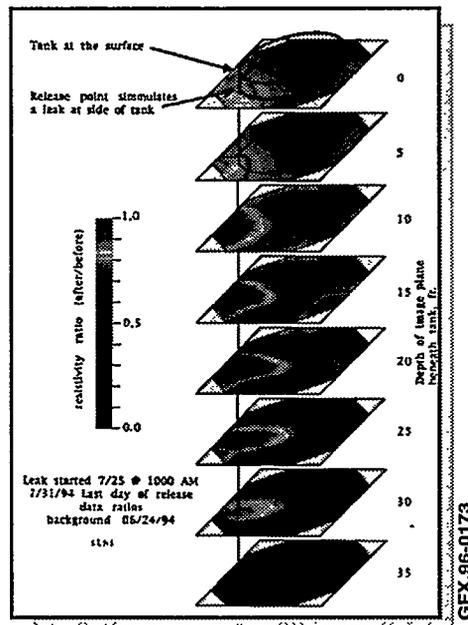


Figure 2.1-1 The figure shows a series of two-dimensional, horizontal tomographs which show the decreases in soil electrical resistivity below a metal tank at the 200 East area of the Hanford reservation. The location of the release point and the outline of the tank's perimeter are shown for reference. The tomographs show resistivity decreases where a salt water solution invaded the soil.

Imaging NAPLs at the OGI LEAP tank is a new task. The tank was prepared for the experiment in early spring of 1995, the experiment was conducted in the summer of 1995, and the tank cleanup will be accomplished (and funded) in FY96. The experiment consisted of releasing a DNAPL (PCE) into a water-saturated sandy loam that has two low-permeability clay layers to impede downward movement. Before, during, and after the release, ERT images were made of both resistivity and chargeability.

TTP INFORMATION

Electrical Resistance Tomography For Subsurface Imaging technology development activities are funded under the following technical task plan (TTP):

TTP No. SF24C223 "Electrical Resistance Tomography For Subsurface Imaging"

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2.2

ACOUSTIC CHARACTERIZATION OF WASTES IN DOUBLE-SHELLED UNDERGROUND STORAGE TANKS

TECHNOLOGY NEED

Information about material properties in underground storage tanks (USTs) is currently provided by intrusive methods such as core sampling, buoyancy-based density measurements, level tapes, and video cameras. None of these methods are effective in determining the distribution of waste types and submerged objects beneath the surface of the waste. In the planned effort to pump the waste out of double-shelled underground storage tanks (DSTs), vitrify it for permanent disposal, and then transfer single shell tank (SST) waste to the DSTs for interim storage, process monitoring will be very important. Critical data will include but will not be limited to, radius of cleaning from the mixer/transfer pump, locations of submerged objects, and density of waste mixtures. The absence of such data could compromise adequately designing a pump, predicting the effectiveness of transfer through lines without plugging, determining how completely a tank has been cleaned, and determining if obstructions or debris in the tank will interfere with pumping. An acoustic method, such as is being addressed in the current work, shows considerable promise of meeting these data needs, which cannot be met by known alternative remote sensing instruments.

TECHNOLOGY DESCRIPTION

This project is developing an acoustic monitoring array to locate and characterize wastes and submerged objects in high-level waste USTs. Two sensors are being developed to comprise a monitoring system: an echo sounder for locating interfaces and tank obstructions, and a density monitor for reporting changes in mixed fluid density during waste mobilization procedures. The array is designed to consist of multiple echo rangers and one or more density monitors mounted directly to the mixer pump. A possible alternative scheme would have sensors deployed through tank risers. Transducers produced for commercial and sport fishing use have been modified to tolerate the high pH, high temperature, and radiologically hot environment in DSTs at the Hanford site. A signal source for making the sonar measurement has been obtained commercially and has been modified to fit the smaller scale and more attenuative environment than as specified for sea water conditions. The density monitor is being developed using the adapted transducers with standard laboratory signal sources and data acquisition equipment. A density monitor and echo rangers have been delivered to the Hanford site and mounted on a mixer pump installed in DST-AN-107. Evaluation of the sensors to measure sludge layer depth, dispersion of the sludge under stirring, changes in supernatant density, effective cleaning radius, and location of

in-tank structures is in progress, and is scheduled to continue through FY96. The prototype monitoring system will be used by Hanford with Ames Laboratory support during the development period. A more automated monitoring system based on FY96 results is being considered for the test/demonstration of a functional test planned to occur in DST-AZ-101.

BENEFITS

Acoustic monitors will directly facilitate the remediation effort in USTs throughout the United States. The sensors promise to be applicable to any fluid-filled tanks, and as more systems are operated in actual tanks, further development of the data acquisition and control system will allow the technology to be fine-tuned for use in a range of waste types. These systems will, in addition to benefiting the remediation process by monitoring mixing and transfer, provide information to aid in designing the most effective transfer pumps. The sensors are installed as part of the mixer/transfer pump and are operated remotely, which minimizes worker exposure for obtaining monitoring data. Also, since the sensors are expected to survive the environment in the tanks, disposal costs are included in those for the pump at decommissioning. Another benefit is that the remote control of the technology could be extended to be operated through a central control station; for example, via Ethernet control of IEEE instruments, or by modem control using commercial remote control software. This would decrease the cost of monitoring by reducing the number of data acquisition control centers, which are currently expected to be one per tank.

COLLABORATION/TECHNOLOGY TRANSFER

Airmar Technology, Raytheon, and Westinghouse Hanford Company have collaborated extensively with Ames Laboratory and Iowa State University on the development of this technology. Westinghouse has cooperated in installing and providing engineering support for tests of the instruments in actual tanks. We estimate they have supplied 0.5 person-years of support in this effort, and have paid for the majority of the installation and safety assessment costs. Airmar has collaborated with Iowa State university researchers to redesign two of their off-the-shelf sensors, choosing robust housings and an appropriate array of piezoelectric elements for use in this application. This company is a small business, but produces a large share of the transducers currently used in hobby and commercial fishing for navigation and fish-finding. Airmar has expressed interest in manufacturing and marketing the finished device, and has the resources needed to handle the job. Raytheon manufactures the pulser used to drive the echo ranging transducers. Engineers at Raytheon have been very cooperative in helping modify the pulsers to be used in the tank environment and by providing engineering drawings and consultations. Raytheon is currently not interested in marketing the device, but is interested in supporting the work as it has in the past. Current planned tests

will initially benefit the development of the instruments and, in addition, will place instruments in tanks that will be used operationally to their full capability as soon as feasible.

ACCOMPLISHMENTS

The sensors in AN-107 have successfully observed the tank wall, risers in the tank, a sludge supernatant interface, and small scale motion in the supernate. The direct density, phase shift, and sound speed data, which allow calculation of density changes with the density monitor, indicate that in-tank density changes will be observable. Sensors developed in collaboration with a manufacturer have been deployed in an actual waste tank for over two years, without failure. These sensors are the only acoustic sensors designed and field tested for tolerance to actual conditions in the high-level waste UST environment. Further tests of the echo ranging and density monitoring instruments in a DST are scheduled for early July 1996. Previous deployment of similar instruments in DST-SY-101 succeeded in demonstrating the survivability of the sensor, and the response of the density monitors to changes in tank density during pumping, but the echo rangers were not operated until after considerable tank mixing, and were not useful in interface detection.

TTP INFORMATION

Acoustic Characterization of Wastes in Double-Shelled Underground Storage Tanks technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. CH14C212 "Acoustic Characterization of Wastes in Double-Shelled Underground Storage Tanks"

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2.3

INFRARED ANALYSIS OF WASTES

TECHNOLOGY NEED

DOE has an inventory of 250 million kilograms of low-level nitrate salt waste and large inventories of other granular or powdered low-level mixed wastes. Presently, low-level mixed waste is immobilized by cementation, but cement-based processed waste cannot contain more than 20% (by weight) salt and still pass the Toxicity Characteristic Leaching Procedure (TCLP). In addition, certain waste chemistries affect the cement, preventing curing or causing expansion that bursts the waste containers. Polyethylene microencapsulation is an alternative promising waste immobilization technology being actively developed at Rocky Flats Environmental Technology Site. Polyethylene microencapsulation can produce a stable waste form containing up to 65% (by weight) waste.

Maintaining both proper immobilization and the highest possible waste loadings requires monitoring the process in real time. The project is using Transient Infrared Spectroscopy (TIRS) as the basis for an on-line, real-time composition monitor of the molten waste stream produced by the encapsulation process. The monitor provides data that will guide the waste process operators in their control of the encapsulation, will document the processed waste composition for certification purposes, and will provide a record of the processed waste should questions or problems later arise. Potentially, TIRS can also be applied to other waste processing operations, such as vitrification.

TECHNOLOGY DESCRIPTION

TIRS is a noncontact, on-line analysis technique for process streams of solid or viscous-liquid material. TIRS provides a real-time chemical (molecular) analysis of the process stream. Figure 2.3-1 shows how the TIRS monitor works. The surface of the molten encapsulated waste stream is cooled by a small air jet as it passes through the field of view of an infrared spectrometer. The stream radiates infrared by virtue of its high temperature. The alteration in the observed infrared spectrum caused by the cooling jet is used by the computer to derive the stream composition, or any other composition-related property. This project within the Mixed Waste Characterization, Treatment, and Disposal Focus Area (MWFA) applies TIRS to monitoring the waste loading in the encapsulated waste stream. Numerous on-site demonstrations of the technology involving several different wastes have been performed, during which a precision of better than 1% by weight was typically achieved. Figure 2.3-2 compares the TIRS analysis results with the known stream composition during one of those demonstrations. A TIRS monitor was built in FY96 for permanent installation at Rocky Flats, and personnel were trained in its operation.

BENEFITS

Polyethylene encapsulation produces a high quality waste form for long term storage or landfilling. The high waste loadings offer substantial cost savings, but the loading must be monitored to ensure the highest (i.e., most economical) loading consistent with proper immobilization. Without on-line monitoring, the waste loading cannot be strictly controlled and the target waste loading would have to be lowered to assure that it did not exceed the maximum allowed level. TIRS is the only technology that can provide on-line, real-time monitoring of the molten processed-waste stream composition. It does this automatically, without contacting the waste stream (except with air), so there is no secondary waste, no worker exposure, and little worker time required. The monitor log can also aid in waste certification, possibly reducing the amount of testing (e.g., TCLP) required.

COLLABORATION/TECHNOLOGY TRANSFER

In FY96 a TIRS monitor was permanently installed at Rocky Flats Environmental Technology Site, and personnel trained in its operation. In previous years, numerous demonstrations involving TIRS and polymer encapsulation, some of them public, were held at Brookhaven and Rocky Flats. In collaboration with Savannah River, we are exploring the application of TIRS to waste-vitrification monitoring. Plutonium and samarium in the vitrification glass produce distinct spectra, and appear to be monitorable. We are investigating the preliminary engineering necessary to apply TIRS to vitrification. TIRS was invented by the

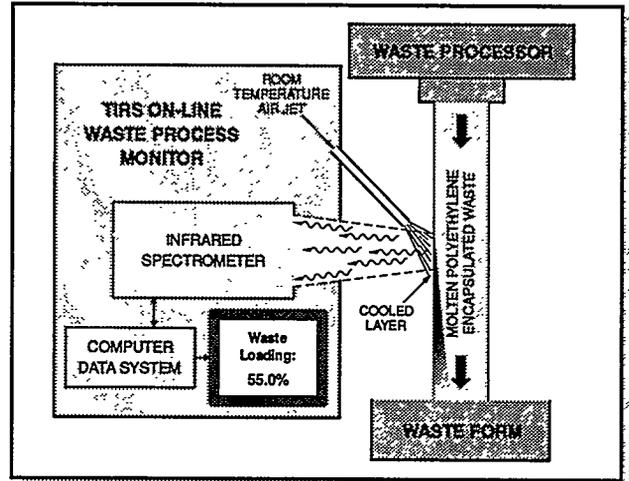


Figure 2.3-1 Schematic of the TIRS monitor on a waste encapsulation line.

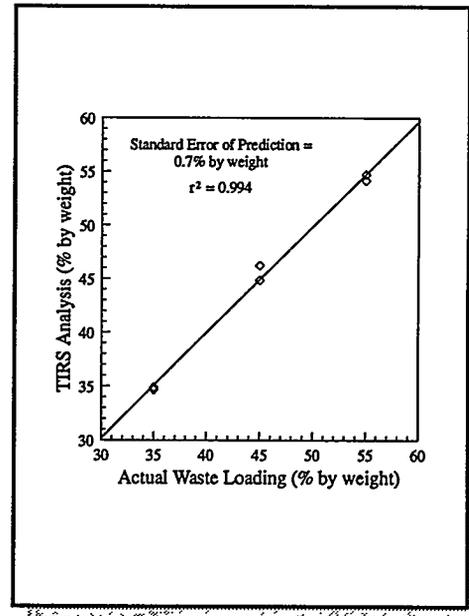


Figure 2.3-2 TIRS analysis compared to the actual loading of low-level nitrate-salt waste in an encapsulated-waste process stream.

principal investigator and is patented by Iowa State University. DOE and its contractors do not require a license to use TIRS, and licensing is available for others. Demonstrations of TIRS for other process applications have been conducted on manufacturers' process lines. Ames Laboratory and Iowa State University received a 1992 "R&D 100 Award" for TIRS.

ACCOMPLISHMENTS

- First hot test; on-site test of TIRS technology on an encapsulation line processing real low-level mixed waste, Rocky Flats, April 1995
- Public demonstrations of the polymer encapsulation and TIRS technologies, Rocky Flats, May 1995
- Successful on-site test on four different waste stream types (e.g., molten-salt oxidation waste, flyash), Rocky Flats, September 1995
- Delivery of a TIRS monitor to Rocky Flats for permanent installation, March 1996
- Training of Rocky Flats personnel in operation of TIRS monitor, April 1996

TTP INFORMATION

Infrared Analysis of Wastes technology development activities are funded under the following technical task plan (TTP):

TTP No. CH13C231 "Infrared Analysis of Wastes"

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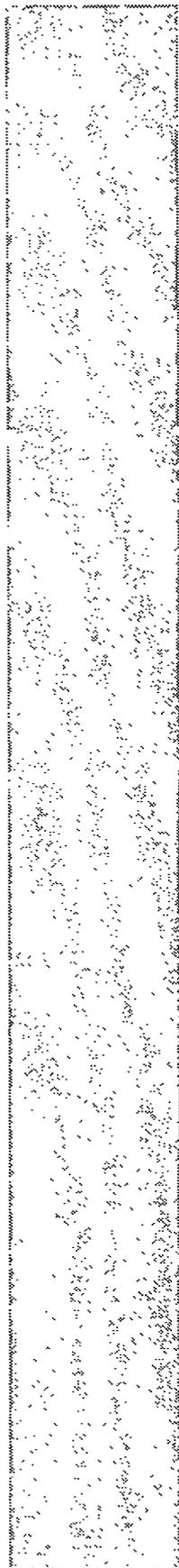
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2.4

NEURAL NETWORK RAMAN CONE PENETROMETER SIGNAL EXTRACTION AND ENHANCEMENT

TECHNOLOGY NEED

The need for in situ chemical characterization of the Hanford tank wastes are driven by both data quality objectives (DQO), and safety and operational considerations. Safety drivers include the monitoring of organic chemical and oxidizer levels to address energetics and flammability; nitrate and nitrite levels with regard to corrosion concerns; plutonium levels to address criticality prevention specification limits; and chemical detection of organic and inorganic species to identify chemical compatibility hazards, including ferrocyanides, nitrates, sulfates, carbonates, phosphates, and other oxyanions. Operational concerns include the monitoring of phosphate levels, driven by the potential formation of sodium phosphate crystals that will increase the viscosity of the waste by formation of a gelatinous matrix that will reduce the ability of pumps to transfer and retrieve waste. A fiber optic remote Raman chemical sensor system will be incorporated and deployed in the Applied Research Associates (ARA) in-tank cone penetrometer to address these chemical safety and operational DQO needs. While Raman is a powerful technique for characterizing chemical species based on their vibrational spectral signatures, it suffers from inherently weak signals and interferences from sources of spectral noise as shown in figure 2.4-1, including fluorescence, fiber optic silica Raman signals, and random charge coupled device (CCD) detector noise. Additionally, the tank analytes of interest are found in a complex chemical matrix that include overwhelming amounts of other materials. These materials may act as potential interferents in a measurement by giving rise to extraneous signals that yield complicated spectra that are difficult to interpret. The neural network (NN) package, jointly developed by Lawrence Livermore National Laboratory (LLNL) and an industry partner, Physical Optics Corporation (POC), will address these issues, providing on-line, real-time chemical identification and analysis to address DQO concerns. This approach uses on-line intelligence to overcome limitations in the signal to noise ratio of instrumentation, and to minimize the effect of interferents in the sample matrix without involving chemical or chromatographic preprocessing of samples.

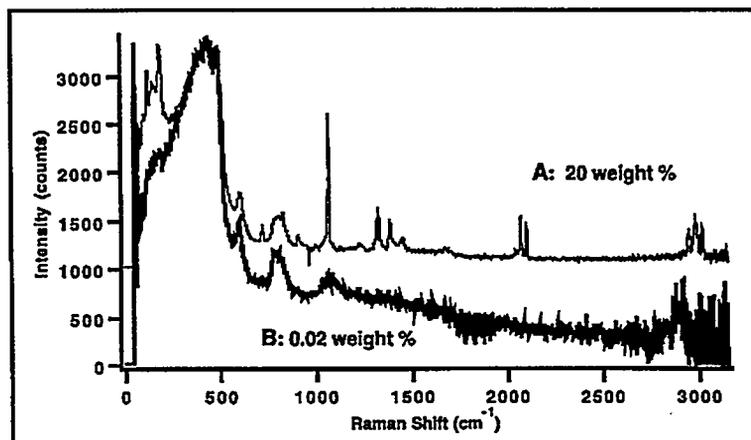


Figure 1: Raman spectra of tank waste simulant consisting of sodium nitrate, sodium nitrite, EDTA, sodium phosphate, and sodium ferrocyanide at 20 and 0.02 weight percent per component. The 20% spectrum exhibits multiple peaks due to the complex mixture. The 0.02% spectrum (bold) illustrates the obscuring of real Raman signal by system noise and silica fiber Raman (broad peaks).

GFX.96-0174

Figure 2.4-1 Raman spectra of tank waste simulant consisting of sodium nitrate, sodium nitrite, EDTA, sodium phosphate, and sodium ferrocyanide at 20 and 0.02 weight percent per component.

TECHNOLOGY DESCRIPTION

The goal of this effort is to produce and deliver a plug-in hardware module that enhances the capabilities of the Raman technique by performing signal extraction, automatic signal analysis, and feature identification on-line and in real time (one second or less per spectrum), in support of the in situ Raman cone penetrometer for chemical characterization of the Hanford underground storage tanks (USTs). The NN is utilized to identify and measure tank chemical constituents identified as safety and operational concerns to satisfy DQO that have been defined for UST waste retrieval and remediation efforts. The NN hardware is developed collaboratively with POC as a continuation of a project funded in FY94 by the Strategic Environmental Research and Development Program (SERDP) for the identification and enhancement of the Raman spectral signatures of chlorinated hydrocarbon solvents.

POC's NN system for the on-line analysis of tank waste component Raman spectral features is a pattern recognition system that combines conventional image processing and feature extraction methods with a proprietary hybrid NN. The neural network draws upon algorithms supplied by chemometrics, principal component analysis, cross correlation, acoustics, sonar, image processing, and oil exploration for a front end preprocessing package. These preprocessing algorithms are used to extract information from the complex raw spectral data, reducing large data sets to information on shapes, locations, intensities, ratios, and slopes of spectral features. The condensed features are fed into the input neurons of the NN for nonlinear processing and algorithms and NN architecture for identifying and measuring tank waste materials. LLNL

is providing POC with the necessary Raman training spectral data for preprocessing algorithm and NN architecture development and optimization. These data consist of individual chemical components in concentrations ranging from 100 to 0.1 weight percent in both solid and aqueous matrices. These concentration ranges cover the concentrations of interest, as required by the waste tank retrieval and remediation DQOs. The tank constituents that are used for training the NN system for real time identification have been selected from the tank DQO lists and include, but are not limited to, sodium nitrate, sodium nitrite, bismuth phosphate, sodium carbonate, sodium sulfate, uranyl nitrate, sodium ferrocyanide, sodium nickel ferrocyanide, edta, tributylphosphate, acetone, sodium formate, dibutylphosphate, ammonium nitrate, sodium chromate, sodium dichromate, butanol, dimethylamine hydrochloride, formamide, sodium aluminate, sodium cyanate, and kerosene. POC is refining the NN package as needed to provide detection limits of tank constituents to necessary limits, greater than or equal to 0.1 weight percent.

BENEFITS

A cone penetrometer-deployed Raman probe offers the great advantage of in situ chemical analysis and depth profiling of tank wastes without the prior removal of waste materials. This greatly reduces the risk of contamination due to sample transportation and handling, minimizes exposure of personnel to radioactive contaminants, significantly reduces or eliminates sample waste generation, and provides significant cost savings. The current costs of obtaining and analyzing a single 18 inch core sample from a high level waste tank costs up to \$750k per core. A data analysis package specifically designed for the analysis of concern for the safety and operational teams at Westinghouse Hanford Company (WHC), will add the benefit of greatly reduced data analysis time and cost. Operational data will be available as soon as it is recorded, rather than after a time delay to allow for post-collection processing analysis.

COLLABORATION/TECHNOLOGY TRANSFER

The original neural network technology was developed by POC under a previous contract to the Army for target pattern recognition, and to SERDP for chlorinated hydrocarbon solvent analysis. The application of the neural network to the Hanford tank farm environment will be a joint venture between LLNL and POC. POC will continue to hold the license to the neural network technology. The development will continue under this program as an in-house program at POC, leading to eventual commercialization of the hybrid neural network for use in government, industrial, academic, and medical communities.

ACCOMPLISHMENTS

The NN was trained to identify the Raman spectra of individual volatile organic compounds such as CCl_4 , CHCl_3 , CH_2Cl_2 , TCE, and TCA during FY95 under SERDP FY94 funding. The training of the NN was accomplished using single component Raman spectra with signal to noise ratios in the range of 5:1 to 35:1. Once the training was complete, the neural net was asked to identify approximately 75 low S/N (1:1 or less) spectra of individual chlorocarbons and four and five component chlorocarbon mixtures that represented complicated spectra with overlapping spectral features. The NN gave correct identifications with 93 percent accuracy, and gave 100 percent rejection of spectra consisting only of noise. Only 30 milliseconds were required to perform a complete deconvolution of 1024 spectral data points, including composition identification. The NN was also able to positively identify 2500 ppm (V/V) CCl_4 in methanol with 100 percent confidence, and 250 ppm (V/V) with 65 percent confidence. This represents an enhancement of the detection limits of CCl_4 by Raman spectroscopy by two orders of magnitude.

TTP INFORMATION

Neural Network Raman Cone Penetrometer Signal Extraction and Enhancement technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. SF26C215 "Neural Network Raman Cone Penetrometer Signal Extraction and Enhancement"

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2.5

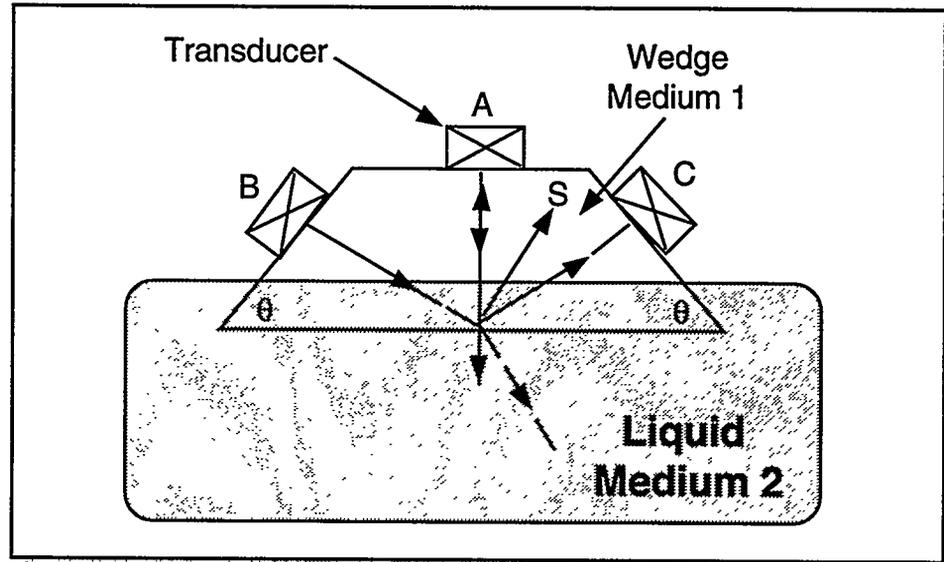
IN SITU SENSOR DEVELOPMENT: ULTRASONIC DENSITY MEASUREMENT PROBE

TECHNOLOGY NEED

All DOE sites with radioactive wastes stored in tanks need to measure density of the waste supernate, the mixed layer, and the settled sludge, to characterize the waste and to ensure that waste is sufficiently mixed and meets criteria to sustain transport prior to pumping waste from the tanks. The ultrasonic reflection coefficient sensor can be used to meet these DOE needs to measure bulk density in tanks and during transport in pipelines. Accurate measurement and tracking of density and density variation in real time provide the potential to control the transport process and to sustain steady transport without transport line blockage. This task supports the US DOE TFA need for real-time measurement of slurry density in-tank and during pipeline transport. In situ density measurements, in the supernatant and mixed layer, provide a profile of the waste density as a function of elevation. These measurements are useful in several applications: to profile the supernate and mixed layer prior to selection of mobilization and retrieval technology, and to profile the supernate and mixed layer during mobilization and retrieval to provide real-time monitoring of the density profile changes during mobilization and retrieval. As the profile reaches a steady state, the success of mobilization and mixing can be quantified. A constant profile shows a fully mixed tank. A profile that varies with elevation shows a stratified tank. Real-time analysis of this data will provide feedback during waste mixing to ensure that waste is retrieved for transport only when it meets the transport criteria. Density measurements can also be used to monitor solids settling, sludge washing, and pretreatment operations.

TECHNOLOGY DESCRIPTION

This project is developing an in situ technique to measure fluid (liquid and slurry) density in vessels and in pipelines. The sensor can be used to measure density with real-time measurement update. The method is based on the reflection coefficient of the ultrasonic signal as it passes through a wedge and impacts the slurry to provide data to calculate slurry density. The bottom surface of the wedge must contact the fluid whose density is to be measured. Alternatively, the sensor can be submerged in the fluid, if this is advantageous. Sensor operation is described in Figure 2.5-1



GFX-96-0175

Figure 2.5-1 Reflection Coefficient Sensor Configuration

The transducers operate at an ultrasonic frequency of a million cycles per second. Ultrasound emitted from transducer A travels through the wedge material and strikes the wedge-fluid interface; part of the signal is reflected and travels back to transducer A, producing a voltage signal or echo; part of the signal is transmitted into the liquid. Similarly, when the ultrasound from transducer B strikes the wedge-liquid interface: 1) some is reflected to transducer C producing a voltage signal, 2) some of the longitudinal wave mode converts to a shear wave, and 3) some is transmitted into the liquid. The double arrows along the direction of the ray indicate longitudinal waves and those perpendicular, shear waves. The signals of interest are those reflected back to A and received by C. In both cases, the reflection coefficients are obtained by comparing the voltages on the transducers when the bottom surface is in contact with a liquid to a reference measurement made in air.

The reflection coefficients depend upon 1) the density of the wedge, 2) the speed of the longitudinal wave in the wedge, 3) the speed of the shear wave in the wedge, 4) the angle at which the ultrasound beam strikes the surface, 5) the speed of the longitudinal wave in the liquid, and 6) the density of the slurry or liquid. Only the last two of these quantities are unknown. By measuring two reflection coefficients from transducers A and B, one has two equations with two unknowns, and therefore the density of the liquid and the speed of sound in the liquid can be determined.

Experiments to verify this technique were performed using solutions of sugar in water, 2-propanol, paraffin oil, trichloroethane, and slurries consisting of silicon dioxide particles (0.0015 in. diameter) in water. Density measurement uncertainties were less than 3%. For slurries, the ultrasonic wavelength is many times the diameter of the particles; individual particles cannot be resolved, and the ultrasound senses an average density.

The task objectives in FY96 are to develop an in situ ultrasonic sensor to measure slurry density in tanks and during pipeline transport, and to demonstrate this sensor during nonradioactive transports tests using waste simulants. Objectives in FY97 are to complete a radiation hardened probe and to conduct a radioactive demonstration in-tank and/or in-pipeline at a site to be selected. The objective in FY98 is to transfer the technology to the private sector to commercialize the ultrasonic density measurement system for radioactive in-tank and pipeline density measurement.

BENEFITS

This sensor provides a simple in situ method to measure slurry or liquid density in real time. Real-time, in situ density data of liquids, and slurries inside waste storage tanks and in pipelines can be used to characterize wastes prior to and during mixing and transfer operations to provide process monitoring and control. Multiple sensors arranged over a range of elevations can provide stratification or settling information.

There are several advantages to this reflection coefficient method. One novel feature of this method is that it can measure the density of very attenuative slurries. Secondly, the voltage on the transducers can be low (on the order of 30 V) because the signals travel only a short distance; this is important for safety considerations. Thirdly, no previous laboratory calibration measurements are needed because the density is determined directly.

COLLABORATION/TECHNOLOGY TRANSFER

Sensor development is occurring at Pacific Northwest National Laboratory (PNNL). Selection of a site for radioactive demonstration of the technology in FY97 is underway. A patent application has been filed for this technology. The technology is available for licensing.

ACCOMPLISHMENTS

- This project was initiated in March 1996.
- A patent for the technique was filed in April 1996.

TTP INFORMATION

The In Situ Sensor Development: Ultrasonic Density Measurement Probe technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. RL36C214 "In Situ Sensor Development: Ultrasonic Density Measurement Probe"

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2.6

ULTRASONIC SENSORS FOR IN SITU MONITORING OF PHYSICAL PROPERTIES

TECHNOLOGY NEED

An estimate of 381,000 m³ of radioactive waste with a radioactive decay of 1.1 billion Ci are stored in high-level waste tanks at Hanford, Savannah River, Idaho National Engineering Laboratory (INEL), and West Valley facilities. These nuclear wastes have created one of the most complex waste management and cleanup problems facing the United States. Release of radioactive materials to the environment from underground waste tanks requires immediate actions of cleanup and waste retrieval. Hydraulic mobilization with the use of mixer pumps will be the process used to retrieve waste slurries and salt cake from storage tanks. To ensure that transport lines in the hydraulic system will not plug, the physical properties of the slurries must be monitored. Characterization of a slurry flow needs reliable measurements of slurry density, mass flow, viscosity, and volume percent solids. The measurements are preferably made with on-line, nonintrusive sensors that can provide continuous real-time monitoring.

TECHNOLOGY DESCRIPTION

Nonintrusive ultrasonic techniques, which have already been widely applied to industrial process controls, are the base technology for this proposed sensor development. Two ultrasonic sensors will be developed and field demonstrated in this project. One is a nonintrusive ultrasonic viscometer for on-line fluid viscosity measurement, and the other is an ultrasonic imaging system for monitoring the volume percent of solids in waste transport lines. Both sensors will be applied to in situ measurements, thus, the sensors will be designed to adapt the process conditions that are corrosive and radioactive. The proposed design of the sensor configuration will consist of two circular arrays of ultrasonic transducers, shear and longitudinal. Each sensor array uses special purpose wedges for transducer mounting. The wedges provide transducer isolation from the process stream and self-calibration capability. The design and measurement principles of the two sensors are described below.

Ultrasonic Viscometer

An ultrasonic viscometer was developed at Argonne National Laboratory (ANL) and was the recipient of an R & D 100 award in 1994. The basic design consists of a pair of ultrasonic transducers mounted on the special purpose wedges. The wedge has a design of two reflection surfaces. One surface is in contact with the fluid being monitored, and the other is exposed to the air. Reflected signals from the two surfaces are measured. The signal amplitudes

(phase changes are negligible) are used to calculate the reflection coefficient of the fluid. Signals reflected from the air side of the wedge represent the total reflection, and thus can be used as reference signals to provide continuous on-line calibration. The Ultrasonic reflection coefficient, R , can be related to ultrasonic impedances of the fluid (Z) and wedge (Z_w) by the relationship of:

$$R = (Z - Z_w) / (Z + Z_w).$$

Since Z_w is a wedge constant, the reflection coefficient measurement gives a direct measure of the fluid impedance. Ultrasonic impedance depends on the type of ultrasonic wave utilized. For the present applications, we consider only acoustic and shear impedances, the former relates to longitudinal mode and the latter corresponds to shear mode. Shear impedance of fluid is given by the square root of the product of fluid density and viscosity. Hence, measuring shear impedance alone does not give a direct measurement of fluid viscosity; another independent measurement is needed to determine the fluid density. This can be achieved by measuring the acoustic impedance of the fluid, which is defined as the product of fluid density and sound velocity. Therefore, the basic design of the viscometer requires both longitudinal and shear wave transducers. The Pulse-echo method is the measurement technique. Longitudinal-wave operation measures sound velocity (V) and acoustic impedance (Z_l) of the fluid, from which fluid density ($\rho = Z_l/V$) is determined. Because fluids do not support shear motion, only the fluid shear impedance (Z_s) can be measured. However, the shear viscosity (η) can be deduced from

$$\eta = (Z_s)^2 / \rho \omega,$$

where ω is the angular frequency. The performance of the ANL viscometer has been evaluated, and at present, the viscometer is applicable only to high viscosities. The design must be modified to allow application to low viscosities (less than 30 cP). This modification is to be the focus of development in the proposed project.

Sensor for Volume Percent Solids

On-line measurement of solids concentration in a solid suspension is very difficult. Resolving particle size distribution is even more complex. Ultrasonic methods have been commonly used for on-line monitoring of solid/liquid flows. At present, ultrasonic flowmeters based on the Doppler or cross-correlation effects have been well developed and applied to flow monitoring. But reliable methods to measure solid concentration have not been established. Some empirical relationships that relate ultrasonic velocity and attenuation to solid concentration have been reported.

Attenuation of ultrasonic waves propagating in homogeneous coal slurries of concentration up to 30% by volume was measured at ANL and the result exhibits a nonlinear dependence on solids concentration. In principle, ultrasonic attenuation is affected by thermal, viscosity, and scattering effects. Therefore, attenuation measurement tends to over-estimate the percent solid

concentration. It has also been observed that the presence of solid particles, particularly of high concentration, may focus ultrasonic waves in the forward direction, thus introducing error in attenuation measurement. Perhaps a better approach is to measure the scattering patterns and establish a correlation between scattering patterns and solid concentrations. Theoretical studies at ANL have shown some of the pattern variation due to increases of solid particles in the fluid. Therefore, we propose to develop a solids-concentration sensor based on measurements of ultrasonic wave scattering pattern. The sensor will consist of a circular array of longitudinal transducers that will send out ultrasonic pulses and receive the scattered waves. An inverse algorithm will be developed to determine volume percent solids and, potentially, particle distribution in the sensing volume. A preliminary study on ultrasonic flow imaging has demonstrated the feasibility of this concept.

BENEFITS

Treatment of waste at waste processing facilities requires the transfer of slurries between storage tanks. The slurries are typically a complex, multi-phase, and highly stratified mixture of saltcake, sludge, and supernatant. During transfer, transport lines may be plugged because of excessive solids in the slurry. The estimated cost to replace a plugged transport line at Hanford is \$47 million. To avoid the transport lines being plugged, the slurry flow must be maintained in the turbulent flow region which requires a Reynold number less than 22,000, a specific gravity less than 1.5, a viscosity less than 30 cP, and a volume percent solids less than 30. Therefore, in situ measurements of slurry density, viscosity, and volume percent solids will ensure the safe and continuous operation of waste transfer. Major benefits to the overall waste retrieval and cleanup are (1) maintaining safe operation, (2) avoiding costs due to line plugging, and (3) providing waste accountability.

COLLABORATION/TECHNOLOGY TRANSFER

The project will produce two practical on-line flow monitoring sensors that have wide applications in many industrial processes, especially the processes involving solid suspension such as coal and paper/pulp slurries. The ultrasonic viscometer is in the process of technology transfer to the Brookfield Engineering Laboratories, Inc. (BEL), Stoughton, Massachusetts, and an industrial prototype will be built and demonstrated in early 1996. The sensor for volume percent solids measurement will be transferred to the flow-instrument industry at its completion. The sensor can be further developed into a real-time flow imaging system, which will increase its market value and industrial application.

ACCOMPLISHMENTS

Work Element A: Evaluation of transducer wedge design:

- Completed a theoretical model for wedge-material evaluation.
- Completed the wedge design for the laboratory prototype viscometer.

TTP INFORMATION

Ultrasonic Sensors For In Situ Monitoring of Physical Properties technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. CH26C217 "Ultrasonic Sensors For In Situ Monitoring of Physical Properties"

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2.7

IN SITU VISCOSITY AND DENSITY MONITORING USING QUARTZ RESONATORS

TECHNOLOGY NEED

Across the DOE complex, storage tanks containing mixed radioactive and chemical wastes must be cleaned up. This requires development of new monitoring technologies so that tank contents can be properly characterized and the mixed wastes safely transported. The TFA has identified a need for in situ viscosity and density monitors to help optimize tank sluicing operations. The monitors will measure slurry parameters both in the tank volume and in transport lines to minimize water additions needed to effectively pump the waste, and to maintain the turbulent flows needed to avoid pump or line plugging.

TECHNOLOGY DESCRIPTION

The in situ viscosity and density monitor is based on a mature liquid sensing technology that provides a precise, sensitive response proportional to the density viscosity product of a fluid contacting a quartz surface. Excitation of an acoustic wave in the thickness shear mode (TSM) in a quartz crystal viscously entrains the liquid at its surface. Changes in the fluid viscosity or density are manifested in shifts in the crystal resonant frequency and resonance damping. These parameters are measured electrically using network analysis or a specially designed "lever" oscillator circuit. Recently, this technique has been utilized in degradation monitors for jet fuels, sensors for determining the quality of cleaning baths, engine fluid condition monitors for vehicles, and cloud point determination for petroleum products.

Extending this technology to measurements in mixed waste tank slurries requires several developments: (1) determining the performance limitations in simulated wastes and understanding the quartz resonator response to solid particulates in the liquids; (2) determining the radiation and chemical resistance of the resonator, associated electronics, and required packages, and then improving their robustness; and (3) demonstrating prototype systems in the laboratory (scheduled for FY96) and the field (FY97 and FY98). Additional tasks in this project will develop and demonstrate a technique for individual determination of fluid viscosity and density, and new, remotely-operating electronic circuitry for extending resonator viscosity dynamic range, and further improving system radiation resistance. Since a single quartz resonator sensor, as used in most viscosity monitoring systems, responds only to the density-viscosity product of the contacting fluid, a dual resonator system (utilizing one smooth surface resonator and one corrugated surface resonator) will be investigated as part of task four.

BENEFITS

The quartz resonator viscosity and density monitor offers technical advantages not achievable by other state-of-the-art instruments: in particular real-time, in situ monitoring capabilities in a small, low-cost package. An additional advantage is the ability to implement the resonator sensors in array format, either in the same sensor head, or in separate sensor heads at multiple locations. This will enable remote, in situ monitoring at several tank and transport line locations, eliminating uncertainties in pumping operations, speeding the tank sluicing process, and lowering site cleanup costs, all while improving overall personnel safety and reducing environmental risks. Also, this viscosity and density monitor should have a range of applications that extend beyond tank slurry characterization, addressing many needs throughout the DOE community.

COLLABORATION / TECHNOLOGY TRANSFER

Past applications utilizing the quartz resonator fluid monitoring technology generated a high level of commercial interest. Several licenses for particular fields of use are now in place. It is anticipated that commercial interest will remain high for this technology in tank slurry viscosity and density monitoring because of the numerous benefits it offers. Selection of one or more industrial partners to participate in the final developments and demonstrations of this technology application is essential to project success.

ACCOMPLISHMENTS

Project technical work started in November 1995. During this time, an improved version of the lever oscillator circuit that drives the quartz resonator in highly viscous fluids was characterized. The viscosity range improved to less than 1100 cP, which is more than a factor of four increase over previous versions. A matrix test approach for evaluating the response of the quartz resonators to suspended solids in simulated slurries has begun. Solids with particle sizes between 1 and 200 micrometers are mixed in concentrations of less than 60% by weight with base glycerol-water solutions. The base fluids have viscosities ranging from 1 to 60 cP. Each solution or mixture is characterized at temperatures from 20 to 80°C using a reference rotating cup viscometer and the quartz resonator monitor. Preliminary results show nonmonotonic changes in resonator response to increasing concentrations of Bentonite clay (one of the test solids) in water mixtures. Correlations of resonator response to viscosity, density, solid concentration, and shear conditions are being evaluated.

TTP INFORMATION

In Situ Viscosity And Density Monitoring Using Quartz Resonators technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. AL26C213 "In Situ Viscosity And Density Monitoring Using Quartz Resonators"

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2.8

PROCESS MONITORING AND CONTROL: AMMONIA MEASUREMENTS IN OFFGASES

TECHNOLOGY NEED

Ammonia is released during the sluicing removal of Hanford tank wastes and processing of high-level wastes in the Savannah River Site (SRS) Defense Waste Processing Facility (DWPF) offgases. On-line measurements of ammonia are needed to provide operational control, enhance worker safety, and to assure that the release of ammonia will not exceed regulatory limits. Several commercially available techniques have been tested; however, none of these have been proven to be sufficiently robust to monitor ammonia reliably in the presence of high moisture contents typical of both Hanford and SRS operations.

TECHNOLOGY DESCRIPTION

In support of the Tank Focus Area, this project is developing and applying tunable-diode-laser (TDL) absorption spectroscopy as a continuous monitor for ammonia in offgases from SRS and Hanford tank wastes. This technology is also applicable to monitoring offgases in thermal treatment processes that are utilized in the MWFA.

The robust instrument developed by this project will provide on-line ammonia detection that is (1) sensitive, (2) stable, (3) capable of operation at high temperatures in a radiation environment, and (4) not affected by the presence of high concentrations of water vapor and carbon dioxide in the offgas stream.

The method detects gaseous ammonia using optical absorption by vibrational transitions in molecular overtone and combination modes at wavelengths near 1.55 micrometers. The sensitivity of the near-infrared TDL to ammonia is greatly enhanced by a proprietary method involving high-frequency modulation of the laser beam and phase-sensitive detection. The ultra-high resolution characteristics of the TDL source permit the separation of ammonia absorption features from nearby spectral lines, due to either water vapor or carbon dioxide. This is a very large advantage when compared with lower resolution optical techniques, such as ultraviolet absorption spectroscopy, Fourier transform infrared spectroscopy, or nondispersive infrared analysis.

Diode lasers are extremely compact, robust, solid-state devices. Their development by the semiconductor industry allows them to be manufactured by mass production methods, thus greatly reducing the cost of individual diode lasers. Operation in the near-infrared wavelength region permits direct coupling of the laser output into optical fibers, which facilitates transmission of the laser beam and alignment with the off-gas stream or extractive sampling volume. This feature also permits the location of laser and electronic modules

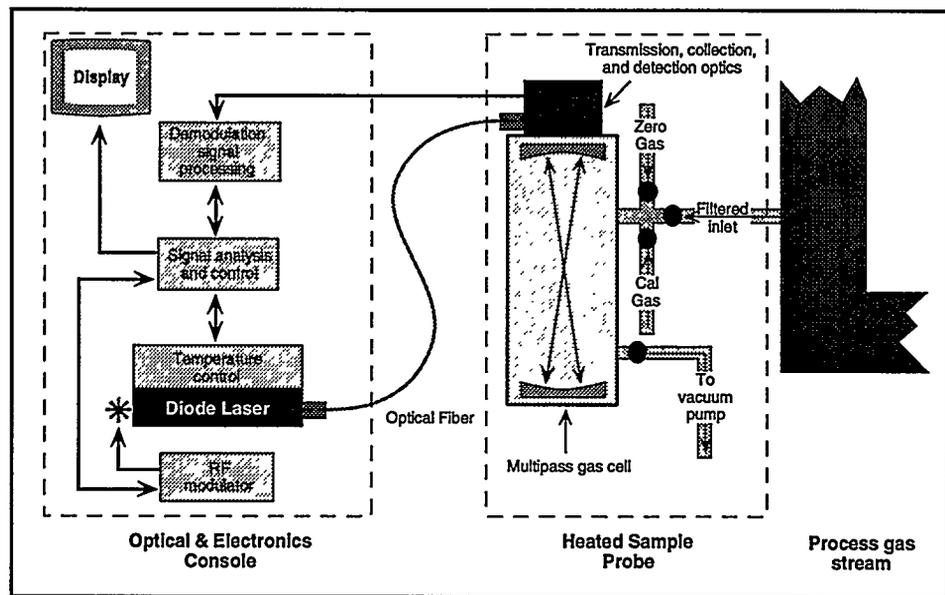


Figure 2.8-1 Experimental layout for the real-time ammonia monitor based on tunable diode laser spectroscopy.

at a safe distance from toxic, hazardous, or radioactive sources. A schematic diagram shown in Figure 2.8-1 illustrates the characteristics of the TDL-based monitor.

BENEFITS

The benefits of near-infrared TDL instrumentation for ammonia monitoring in waste tank treatment are numerous: (1) unambiguous identification of ammonia, even in high moisture and carbon dioxide environments; (2) rapid data acquisition and analysis for process control and demonstration of regulatory compliance; (3) low-cost optical and electronic hardware; (4) physically robust components; and (5) possibility of remote sampling. Real-time analysis for process control can reduce downtime for cleaning by increasing operational efficiency. It can also reduce the time required for regulatory compliance checking and permitting.

COLLABORATION/TECHNOLOGY TRANSFER

Throughout this project, we are working closely with Spectrum Diagnostix (SDx). SDx is currently commercializing an instrument for ammonia detection based on TDL spectroscopy for application in the commercial power-generation industry. We are conducting the research and development necessary to adapt this technology for DOE waste management processes, and to facilitate its rapid commercialization.

ACCOMPLISHMENTS

- SDx tested a TDL ammonia monitor on a continuous basis at three commercial electric power generation plants during FY95. Continuous monitoring of ammonia was done in conjunction with the operation of NOx suppression hardware on gas streams saturated with water vapor and with high concentrations of carbon dioxide. Results demonstrated sub-ppm sensitivity that compares well with independent wet chemical analysis.
- During FY95 we were supported by the Mixed Waste Focus Area in an effort to develop a TDL-based monitor for volatile organic compounds (VOCs). During this period we measured near-infrared survey spectra and ultrahigh-resolution TDL absorption spectra in the 1.65- μm wavelength region for a number of small inorganic molecules and VOCs. For a TDL-based VOC monitor, we estimate good sensitivity for methane, chloromethane, dichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, and vinyl chloride, in addition to ammonia.
- We have established technical contacts at SRS and made plans for initial testing of the TDL-based ammonia monitor on their pilot-scale facility while the construction of the DWPF is completed. Laboratory tests are underway to evaluate potential interference from major species in the process offgas.

TTP INFORMATION

Process Monitoring and Control: Ammonia Measurements in Offgases technology development activities are funded under the following technical task plan (TTP):

TTP No. AL36C216 "Process Monitoring and Control: Ammonia Measurements in Offgases"

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3.0

PROJECTS FOR THE MIXED WASTE CHARACTERIZATION, TREATMENT AND DISPOSAL FOCUS AREA

The critical characterization problem areas for the Mixed Waste Characterization, Treatment and Disposal Focus Area (MWFA) include: determination of the types and amounts of hazardous wastes in sealed containers to permit shipment to the Waste Isolation Pilot Plant WIPP (transuranic waste), or to the appropriate waste treatment train (low-level mixed waste); real-time monitors to enable effective process control of waste treatment, and to verify that off-gas and process streams have acceptably low concentrations of contaminants; and monitors for providing quality assurance that the final waste form meets relevant waste acceptance criteria for ultimate disposal.

Technologies under development for determination of type of waste and amount of contaminants in sealed containers are currently directly under the MWFA, but some of these projects will transition to Characterization Monitoring Sensor Technology Crosscutting Program in fiscal year 1997. In addition, a new project in this area will begin next year.

Five technologies for mixed waste treatment via vitrification were demonstrated by the Diagnostic Instrumentation Analysis Laboratory (DIAL) to determine melt temperature (pyrometer), melt discharge temperature (pyrometer), thermal images of the melt discharge, offgas contaminants (laser-induced breakdown spectroscopy for hazardous metals and Fourier Transform Infrared Spectroscopy for HCl and organics), heavy metals in the molten glass, and offgas flow velocity (laser doppler velocimeter). In addition, a laser spark spectroscopy continuous emission monitor (CEM) for hazardous metal emissions in offgases is under development by CMST-CP. Two new CEM development projects are expected to begin in FY97.

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3.1 DIAGNOSTIC INSTRUMENTATION AND ANALYSIS LABORATORY

TECHNOLOGY NEED

Better and improved monitoring and control methods are needed to optimize the thermal treatment processes, in particular the plasma torch treatment system.

TECHNOLOGY DESCRIPTION

Accurate characterization and control of plasma torch facilities for mixed waste remediation is currently a major effort at the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University. Although plasma torch systems have been used commercially for many years, most notably in material science applications and for the treatment of incinerator ashes, the extension to mixed waste presents challenges. Specific issues are concerned with the composition of the input waste stream, the longevity of torch components such as electrodes and vortex generators, refractory wear, the quality of the final waste form, downstream gas compositions, and the performance of air pollution control devices. Evaluation of these factors requires a systematic approach including instrument development, materials studies, systems integration, modeling, and control system development.

BENEFITS

The DIAL activities support ongoing test facilities and provide improved characterization, monitoring, and control instrumentation systems. They also provide diagnostic field measurements and demonstrations.

COLLABORATION/TECHNOLOGY TRANSFER

Cooperative research and development (R&D) efforts, with an emphasis on mixed waste treatment, are underway with the following participants:

- Westinghouse Savannah River Technology Center, Aiken, South Carolina, and Clemson University, Clemson, South Carolina
- Argonne National Laboratory-West, Idaho National Engineering Laboratory, Idaho Falls, Idaho
- Western Environmental Technology Office, Butte, Montana
- Various industrial affiliates

ACCOMPLISHMENTS

A major thrust of the work is to maximize the torch lifetime from an operational approach, to look at improved electrode materials, and to provide warning of an imminent electrode failure. The overall progress of the DIAL program has also been demonstrated by the activities of the field operations program. The field program is designed for the rapid demonstration and implementation of modern field-ready diagnostic methods for characterization, monitoring, and control purposes.

DIAL's mobile instrument laboratory was used to support a series of measurements on the Transportable Vitrification System (TVS) at Clemson University. At Clemson, exploratory measurements on the TVS focused on determination of the melt temperature, the melt discharge temperature, thermal images of the melt discharge, offgas compounds, the heavy metals in the molten glass, and the offgas local flow velocity and velocity profile exiting downstream of the melters.

The primary objectives of the measurements on the TVS were to: (1) characterize the gas stream at the measurement locations; (2) demonstrate the capability of the measurement technique; (3) provide useful facility data; and (4) enable planning for future tests.

Preparations are underway for a field trip to the Environmental Protection Agency (EPA) test facility in North Carolina. Continuous emissions monitoring of offgas heavy metals will be conducted, and the results will be compared to those obtained with conventional EPA multi-metals methods.

TTP INFORMATION

Diagnostic Instrumentation and Analysis Laboratory technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. CH03C231 "Diagnostic Instrumentation and Analysis Laboratory (DIAL)"

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3.2

SUPPORT FOR RESOURCE CONSERVATION AND RECOVERY ACT METAL AND AIR STREAM CHARACTERIZATION

TECHNOLOGY NEEDS

MSE Technology Applications (MSE-TA), Inc's., support for the Resource Conservation and Recovery Act (RCRA) Metal and Air Stream Characterization Project is comprised of one task: to select a test bed and evaluate the performance of field transportable technologies in the identification and quantification of RCRA and other heavy metals in soils. The primary objectives of this technology demonstration were to: (1) select and characterize two demonstration sites, (2) select technologies for the demonstration, (3) verify developer claims regarding technology performance, (4) compare field instrument performance to conventional Environmental Protection Agency (EPA) approved laboratory analytical methods and protocols, and (5) determine the logistical and economic resources required to operate each technology demonstrated.

TECHNOLOGY DESCRIPTION

Technology developers involved in the RCRA and Other Heavy Metals in Soil Demonstration were: (1) Los Alamos National Laboratory (LANL), Laser-Induced Breakdown Spectroscopy (LIBS), (2) Meldok, Inc., LIBS, (3) Pacific Northwest National Laboratory (PNNL), Stripping Voltammetry, and (4) PACE Environmental Laboratory, Flame Atomic Absorption.

LIBS is a form of atomic emission spectroscopy in which powerful laser pulses are focused on the soil sample to form a hot micro plasma. Because of high plasma temperature (8,000 to 10,000 K), material in the plasma volume is vaporized, exciting the atoms and inducing atomized, energized, and consequently, characteristic light emission occurs, with unique spectral signatures. Using appropriate calibration, quantitative analysis is possible.

Stripping Voltammetry is a two-step electroanalytical technique for metals concentration measurement. In the first step, the target metal is preconcentrated onto the working electrode, and in the second step, the accumulated metal is stripped by applying an anodic potential scan. The resultant measured peak current is directly proportional to the metal concentration. Alternatively, a constant current is used to strip the accumulated metal and the voltage versus time plot is recorded. Approximately 30 metals can be measured by electrolytic deposition or adsorptive accumulation of a suitable metal chelate onto the electrode surface.

Pacific Northwest Laboratory used three stripping voltammetry systems to measure metals in soils. Adsorptive stripping voltammetry analysis for chromium was performed using an EG&G PAR Model 264A voltammetry analyzer and a PAR Model 303A static mercury drop electrode (SMDE). Stripping potentiometry analysis for Cd, Cu, and Pb was performed using a PSA TraceLab system with a glassy carbon disk or the ETG Metalyzer 3000 system, which has been developed for the determination of Cd, Cu, and Pb in water.

Flame atomic absorption is the process that occurs as a ground state atom absorbs energy in the form of light at a specific wavelength, and is elevated to an excited state. The amount of light energy absorbed at the specific wavelength will increase as the number of atoms of the selected element in the light path increases. The relationship between the amount of light energy absorbed and the concentration of the analyte present in known standards can be used to determine unknown concentrations by measurement of the amount of light absorbed.

BENEFITS

DOE, along with other federal agencies and private industry, are faced with massive soil characterization problems at numerous contaminated sites. It is anticipated that millions of dollars would be required for laboratory analyses to accurately characterize the constituents in the contaminated soil. DOE is attempting to meet the objective of cost-effective field analyses by developing and demonstrating promising field transportable heavy metals in soils measurement technologies.

COLLABORATION/TECHNOLOGY TRANSFER

Organization and execution of the RCRA and Other Heavy Metals in Soils Demonstration was a collaborative effort among the following participants: MSE-TA, of Butte, Montana, a prime contractor of DOE and responsible for operating the Western Environmental Technology Office (WETO); DOE EM-50 CMST-CP; Ames Laboratory (Ames), a CMST-CP support office; Sandia National Laboratories (SNL), DOE's representative to the CMST-CP and under contract to the EPA to provide technology developers with a clearly defined verification pathway; and the technology developers.

The purpose of these demonstrations is to develop and evaluate technologies that can identify contaminants and/or objects of concern in a field application. Potential users of these technologies are widespread across the DOE complex and in the nation. Because the needs are extensive, the technologies would be readily transferable to private entities. Some candidates for these technologies are Superfund sites, existing operating mine sites, and nonoperating mine sites.

Data generated during these demonstrations will result in dissemination of technical and economic information via presentations and/or publications at national meetings, conferences, workshops, seminars, etc.

ACCOMPLISHMENTS

RCRA and Other Heavy Metals in Soils Demonstration was completed in October 1995. The final report has been written and is scheduled to be distributed in June 1996.

Each technology was evaluated individually, and technology analytical field results were compared to the technology developers' claims and averaged analytical results of an on-site analytical laboratory, an off-site analytical laboratory, and an independent analytical laboratory. Analytical laboratories analyzed duplicate soil samples using conventional laboratory methods. Conventional laboratory analysis data was considered confirmatory. All confirmatory laboratories were to abide by the requirements of the project Quality Assurance Project Plan.

Quantitative and qualitative factors were considered in the design and implementation of the technology demonstration. Quantitative factors included accuracy, precision, and sample throughput. Qualitative factors included portability, ease of operation, logistical burden, and robustness.

LANL LIBS technology participated as a Level 1 technology. This was the first field demonstration for this instrument. Precision of this technology was very good, indicating the instrument's ability to duplicate soil sample analyses consistently. However, the accuracy of the LANL LIBS technology when compared to the confirmatory laboratory analyses was generally greater than their performance claim of 20%. Performance Evaluation (PE) samples had Cr and Cd concentrations that were an order of magnitude higher than the demonstration field samples. For the PE samples, the technology detected Cr and Cd within the performance acceptance limits. This technology performed better on lower concentrations of Mn. Sample throughput matched the developer's claim of two samples per hour.

PNNL's static mercury drop electrode (SMDE) technology participated as a Level 1 technology. This was the first field demonstration for this technology. Precision of the SMDE was lower than the developers claim. Accuracy of the technology was acceptable for the PE samples; however, the instrument was less accurate when analyzing the demonstration field samples. SMDE reported results for the field sample were consistently higher than the values reported by the confirmatory laboratories. Sample throughput was 2 samples per hour, while the developer's claim was 4 samples per hour.

Precision of the PNNL, PSA TraceLab was generally below the developer's claim of 40%. Accuracy was generally above the developer's claim of 20% for Cd and Cu, but below 20% in all cases for Pb. Values reported for Cu were

consistently lower than the confirmatory laboratories results, suggesting a possible calibration error. Sample throughput was two samples per hour, while the developer's claim was four samples per hour.

PNNL's Environmental Technology Group Metalyzer 3000 was a hand-held production model prototype Level 1 technology. The developer did not analyze the PE samples or the mandatory duplicate samples, so it was difficult to assess the precision and accuracy of the technology. The developer did perform a duplicate analysis on one sample, then calculated for this duplicate analysis within the developer's claim of 40%. Accuracy of the Metalyzer 3000 did not meet developer's claims for the samples analyzed. Sample throughput was 3.3 samples per hour, while the developer's claim was four samples per hour.

TTP INFORMATION

Support For RCRA Metal and Air Stream Characterization technology development activities are funded under the following technical task plan (TTP):

TTP No. PE153001 "Support For RCRA Metal and Air Stream Characterization"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

None available at this time.

3.3

SUPPORT FOR RESOURCE CONSERVATION AND RECOVERY ACT METAL, FORENSIC GEOPHYSICS, AND AIR STREAM CHARACTERIZATION

TECHNOLOGY NEED

TASK 1: DIAL requires access to a viable test train and support in test implementation, test analysis, and operational coordination.

TASK 2: MACTEC requires support in field activities such as instrument position. In addition, support in test implementation, test analysis, operational coordination, and reporting is required.

TASK 3: The Center for Process Analytical Chemistry (CPAC) requires access to a viable test train with classical analysis, supports for comparison with results by the flow probe unit. CPAC also requires support in test implementation, test analysis, and operational coordination.

TECHNOLOGY DESCRIPTION

TASK 1: DIAL will use their Fourier Transform Infrared Spectroscopy (FTIR) equipment to measure and verify the performance of the Thermatrix flameless oxidizer. The FTIR method to be used is based on the absorption or emission of infrared radiation as a molecule undergoes a transition from one vibrational-rotational level to another. FTIR is a monitoring device that has the ability to detect organic molecules and break down products that may be precursors to dioxin formation.

DIAL will also employ their LIBS equipment to measure and verify the performance of the Pall ceramic filter. LIBS is a laser-based diagnostic technique for measuring the concentration of toxic metals in the offgas emission from various waste treatment facilities. The LIBS produces a pulsed laser beam that is focused at the test point and produces a spark due to the high-energy density at the laser pulse. The spark generates a plasma that excites various atomic elements present in the focal volume. The atomic emission from the plasma is collected with a collimating lens and sent to the detection system. Wavelength positions of the emission lines are used to identify the atomic species present. Likewise, the intensity of the atomic emission lines observed in the LIBS spectrum are then used to infer the concentration of the atomic species.

TASK 2: Ground penetrating radar (GPR) is a remote sensing geophysical technique for mapping subsurface soils, groundwater, and hydrocarbon plumes, and for locating buried objects such as tanks, pipes, and electrical utilities. The GPR system consists of an antenna, a processing console, a graphic display recorder, and an optional magnetic recorder.

TASK 3: The Flow Probe Chemical Analyzer is an in situ generic chemical speciating technology that measures chemicals in both liquid and gas states for field survey applications, as well as process control and monitoring applications. Applications for this technology are the same as those that use reagent-based, optical absorption spectroscopy. The analyzer was designed to be an in situ generic platform for performing wet chemistry-based analyses in field survey applications and process control and monitoring applications.

BENEFITS

TASK 1: The FTIR system has potential of providing a real-time ability to detect organic molecules and breakdown products that may be precursors to dioxin formation. The LIBS systems has potential of providing real-time measurement of toxic metals in the thermal treatment offgas stream.

TASK 2: The GPR systems will provide rapid assessment of site conditions using noninvasive remote sensing techniques. Data provided by the GPR may improve the success of more standard techniques such as drilling and sampling by allowing specific target areas to be drilled or sampled. GPR can be used to: (1) find buried objects, (2) map subsurface sediments, bedrock, and groundwater, (3) locate areas of contaminated sediments and leachate plumes, (4) identify and map fracture zones, cavities, and voids, and (5) determine the engineering properties of soils and rock, including rippability.

TASK 3: The Flow Probe Chemical Analyzer has the advantage of well characterized reagent chemistry and optical spectroscopy as its detection mechanism. The sensor size is small, with a small analysis volume and a high detection sensitivity (a few parts per billion for many analytes). The analyzer is very efficient, allowing many analyses to be conducted before reagent replenishment and waste extraction.

COLLABORATION/TECHNOLOGY TRANSFER

Potential users of these technologies are widespread across the DOE complex and the nation. Because the need is extensive, the technologies should be readily transferable to private and public entities. Developments from the evaluations will result in dissemination of technical and economic information via presentations and/or publications at national meetings, conferences, workshops, seminars, etc.

TASK 1: The major collaborator on this effort is DIAL. Both the LIBS and the FTIR have applicability in the government and private industry.

TASK 2: The major collaborator on this effort is MACTEC. GPR has applicability in both government and private industry.

spark technology. Sandia is cooperating with Sky+ in their effort to commercialize Sandia's prototype metal emissions monitor. Sandia is also cooperating with Laser Diagnostics (Los Alamos, NM) to evaluate Laser Diagnostics' proprietary method for calibration of laser spark measurements.

ACCOMPLISHMENTS

- Instrument performance specifications (detection limits, species of interest, etc.) have been defined for effluents typical of DOE waste treatment processes.
- Laboratory experiments have been conducted to demonstrate the feasibility of a continuous metals monitor based on the laser spark technology.
- A prototype portable continuous metal emissions monitor based on LASS has been designed, fabricated, and evaluated both in the laboratory and in field experiments.
- The prototype metal emissions monitor system has been demonstrated at a DOE mixed waste treatment experimental facility, the Clemson University Joule Melter Project, where it measured lead, cadmium, and manganese in the effluent stream.
- An upgraded, remotely operable prototype monitor has been developed and has been demonstrated both at a DOE funded, pilot-scale, plasma-processing facility and at the EPA Incineration Research Facility. This prototype includes capabilities to determine metal concentrations in real time and includes a method for calibrating instrument response in the field.

TTP INFORMATION

Metal Emissions Monitor for DOE Mixed Waste Thermal Treatment technology development activities are funded under the following technical task plan (TTP):

TTP No. AL33C231 "Metal Emissions Monitor for DOE Mixed Waste Thermal Treatment"

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4.0

PROJECTS FOR THE DECONTAMINATION AND DECOMMISSIONING FOCUS AREA

Four major Decontamination and Decommissioning Focus Area (D&D) characterization problems require advanced technologies: contaminants inside pipes and enclosed process equipment need to be assayed prior to dismantlement to minimize worker exposure; contaminants on material in rubble piles need to be assayed to facilitate cost-effective, final disposition of the material; flaws in building supports and overall facility structural integrity need to be assessed to ensure worker safety; and airborne and surface contaminants must be detected and monitored in real time with field deployable sensors to demonstrate effectiveness of decontamination and to guarantee worker safety during D&D operations.

Characterization, Monitoring and Sensor Technology Crosscutting Program (CMST-CP) has technologies under development to help address two of these problems. Real-time, field deployable sensors to monitor D&D operations include laser-induced fluorescence imaging of surfaces for uranium and a radiation sensor that can monitor alpha, beta, and gamma radiation simultaneously. The need for assaying hazardous contaminants enclosed inside pipes and process equipment could be addressed by the portable, x-ray imaging system. A project to address rubble piles contaminated with uranium or other radionuclides emitting alpha particles is scheduled to begin in FY97. Only if more money were to become available to CMST-CP would new projects to address the last problem area of facility structural integrity be initiated.

Finally, a new methodology is under development to expedite the characterization process for facilities requiring D&D. If successful, it is anticipated that the time savings and the improved integration of all characterization data would greatly decrease characterization costs similar to the very successful "Expedited Site Characterization" methodology.

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4.1

DEFINING REQUIREMENTS FOR RADIOLOGICAL SENSORS AND ROBOTIC PLATFORM TECHNOLOGIES SPECIAL TECHNOLOGIES LABORATORY CHARACTERIZATION, MONITORING AND SENSOR TECHNOLOGY SUPPORT

TECHNOLOGY NEED

Task 1: The establishment of standards of quality for Office of Science and Technology (OST) programs will provide principal investigators, U.S. Department of Energy (DOE) customers, and DOE program reviewers with guidelines that can be used to evaluate existing and future OST proposals for quality and relevance.

Task 2: Identification of D&D measurements to be made and the platform and sensor problems associated with those measurements, and monitoring the appropriate sensor and platform technologies to ensure mutual compatibility will maximize the specificity of each to D&D measurements.

TECHNOLOGY DESCRIPTION

There is no single technology directly associated with this program since they are several and varied, and are associated with programs currently being monitored and assisted. As a result, the technology description is better replaced with a task description.

Task 1: A document for each new program is prepared in association with the principal investigator. It includes a detailed set of performance specifications for use in reviewing proposals for new and future projects, with each examined for both technical and management contents. New, experimental plans are evaluated for overall technical merit by matching proposed capabilities with requirements to estimate the probability of success. Similar proposals are screened for duplication.

For existing programs, low profile, on-site visits are made to increase the accuracy of technical assessments. Evaluation criteria for each of the programs are established to provide standards for performance comparisons. Sensors and related instrumentation are evaluated for performance expectation, while data processing algorithms are examined for technical merit.

Proposed experimental plans, which include schedules, milestones, cost estimates, objectives, and performance specifications, are reviewed for reality and consistency. These criteria are then used to determine if the measured values meet regulatory requirements, projected milestones have been reached, data are both reasonable and realistic, and the system is performing as expected.

Task 2: Reductions and cessations of activities at nuclear weapon production facilities have generated a need for D&D activities at those sites. Selections of appropriate sensors and sensor systems depend strongly on measurements to be made and robotic platforms under development. This program will monitor the progress of radiological sensor technology development as it applies to D&D requirements.

Results of measurements at selected sites are monitored to evaluate the effectiveness of the sensors in meeting requirements. Deficiencies are noted and analyzed to determine if new and different sensor systems may be required. The results are communicated to OST for review.

Because the D&D requirements are constantly changing, measurement technologies will have to respond accordingly. This program assists OST in monitoring the progress of design, development, and availability of new and innovative sensors and sensor systems. It also assists in testing and evaluation for reliability and applicability. Visits are made to D&D sites to observe measurements to be made and sensor systems to be used. Robotics/sensor system communications are evaluated and monitored to ensure coordinated development. Sensor developments are also monitored to assess their utility in current and future measurements.

BENEFITS

Task 1: The enhanced quality of the OST programs will provide DOE with improved guidelines for evaluating existing and future research and development (R&D) proposals. Improvements in data quality will provide savings in cost and time, and reductions in human risk and waste generation.

Task 2: The enhanced quality of the radiological sensors in D&D applications will provide DOE with improved cleanup capabilities. Depending on the specific programs under evaluation, these improvements will contribute to savings in cost and time, and reductions in human risk and waste generation.

COLLABORATION/TECHNOLOGY TRANSFER

Not applicable for either task.

ACCOMPLISHMENTS

- Developed of the radiological sensor for Site Characterization and Analysis Penetrometer System (SCAPS) to the level where it is ready for a full-scale demonstration.

TTP INFORMATION

Defining Requirements for Radiological Sensors and Robotic Platform Technologies Special Technologies Laboratory CMST Support technology development activities are funded under the following technical task plan (TTP):

TPP No. NV05C261 "Defining Requirements for Radiological Sensors and Robotic Platform Technologies Special Technologies Laboratory CMST Support"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

None available at this time.

4.2

A ROBUST RADIATION DETECTOR FOR RAPID WASTE CHARACTERIZATION

TECHNOLOGY NEED

This project directly addresses several needs for radiation detection including: portable sensors for use on robotic systems for waste and facility characterization; and field deployable equipment for rapid characterization of radionuclides in soil, groundwater, debris, equipment, and process effluents. The chemical vapor deposition (CVD) of a diamond coating on a Cadmium Zinc Telluride (CZT) solid state detector yields a sensor that is impervious to extremely hazardous environments such as corrosive chemicals and high radiation fields. The thin diamond coating detectors are excellent for measurement of alpha and low energy beta particles and since diamond has very low dark currents, they can be expected to operate in ambient light. Standard use of separate handheld gamma ray and alpha particle detectors are inadequate due to excessive worker exposure, high expense of operating these detectors due to long times to cover large areas and the labor costs. Commercial solid state detectors are available for alpha particle measurements but these devices are not solarblind or impervious to corrosive chemicals and high radiation fields.

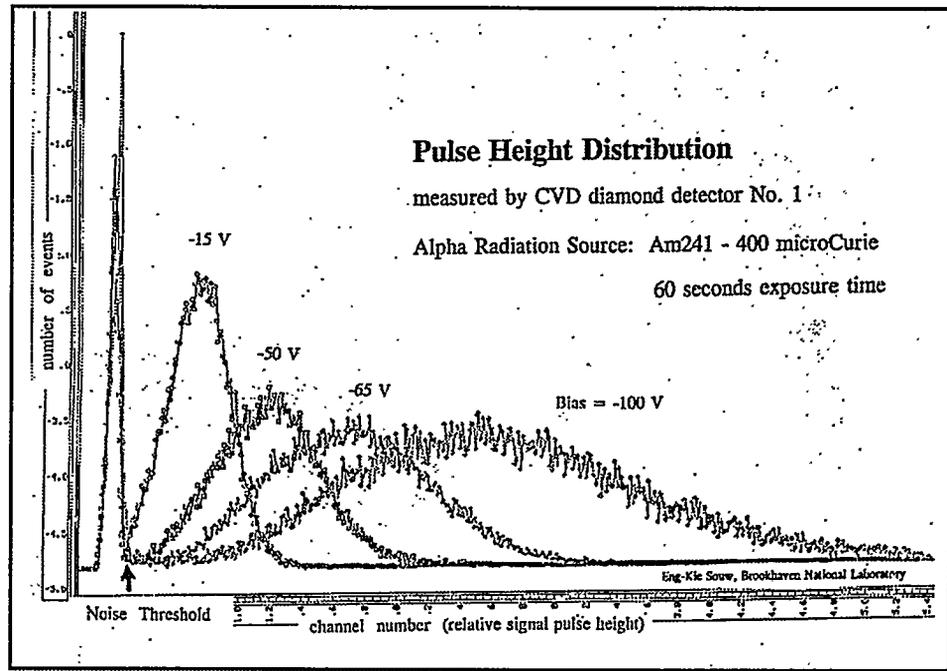
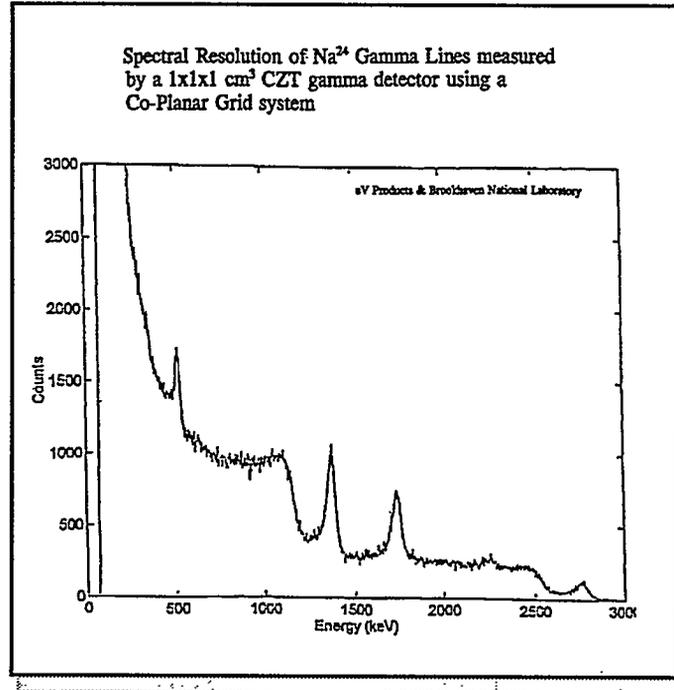


Figure 4.2-1 Pulse Height Distributions measured by a Brookhaven National Laboratory/Northrop-Grumman-made CVD Diamond Detector under 60 second exposure to 400 microCurie ^{241}Am alpha radiation

Figure 4.2-2 Spectral resolution of Na^{24} gamma lines measured in a $1 \times 1 \text{ cm}^3$, eV-manufactured CZT detector with co-planar grid system: The gamma line at 1.3686 MeV is fully developed; the second gamma line at 2.7540 MeV is too energetic for a 1cm-thick CZT wafer (hence, the low efficiency/peak intensity); the pertaining pair-production & double-escape peak appears prominently at 1.734 MeV



TECHNOLOGY DESCRIPTION

To take advantage of the superior properties of diamond in this project, the conventional front electrode of the Standard Solid State detector is replaced by a p-type, boron-doped CVD diamond layer, so that only the diamond, and no metal layer or coating, is exposed to harsh environments.

CZT has been identified recently as being ultimately superior to CdTe with regard to gamma detection properties. To improve spectral resolutions at higher gamma energies, a recently invented co-planar grid (CPG) technology may be applied.

BENEFITS

Robust, miniaturized radiation sensors can be engineered to robotic systems to eliminate worker exposure during surveying of walls, floors, ceilings, process equipment or debris.

Radiation sensors engineered to robotic systems are expected to lower surveying costs by more than a factor of ten by eliminating the need for survey and survey support team in the field and by cutting the time for characterizing large areas by over a factor of five by running robotic systems 24 hours a day.

Chemically robust and radiation-hardened sensors can be deployed into highly restricted facility areas and directly into waste and debris, allowing unique determination of the radiation levels at these sites.

COLLABORATION/TECHNOLOGY TRANSFER

This collaborative project is making use of Northrop-Grumman's plasma-enhanced CVD diamond reactor, as well as their expertise in diamond-growing and vacuum-brazing of diamond films to other materials. The project will also benefit from a collaboration with the N-G radiation detector group and the company's potential for nuclear detector commercialization.

The project (NJIT) is taking advantage of an existing BNL-New Jersey Institute of Technology collaboration between the BNL Principal Investigator and a NJIT Professor in photoluminescence and radiation damage in microelectronics, while making use of a BNL-owned laser and CCD camera installed at NJIT for that purpose.

As soon as the persistent problem with bulk polarization is resolved, a patent application will be filed for a CVD diamond alpha dosimeter. A second patent application on a complete alpha-beta-gamma detector system is planned, pending a successful development of a composite CVD-diamond/CZT device. These patents provides a basis for technology transfer to private industry, with Northrop-Grumman holding the primary license right.

ACCOMPLISHMENTS

- Experimental results indicate that the distribution broadening occurs primarily due to a polarization effect which seems to stop, or at least to slow down substantially, after 11 minutes of continuous exposure under 150 V bias voltage while the pulse height distribution remains well-isolated from the noise background. If results prove reproducible, a diamond detector can be readily used as an alpha particle dosimeter.
- Analysis of gamma spectroscopic performance, with and without the CPG technique, has been conducted on CZT wafers manufactured by three different companies.
- Analysis of current transport and carrier trapping in CVD diamond from photo conductive (PC) current measurements has been carried out at BNL to improve the diamond detector performance and, in particular, to suppress the polarization effect.

TTP INFORMATION

Robust Radiation Detector for Rapid Waste Characterization technology development activities are funded under the following technical task plan (TTP):

TTP No. CH353001 "A Robust Radiation Detector for Rapid Waste Characterization"

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4.3

PORTABLE X-RAY, K-EDGE HEAVY METAL DETECTOR

TECHNOLOGY NEEDS

Cleanup of many DOE facilities requires dismantling equipment that was used to process hazardous materials such as uranium, plutonium, and mercury. Using existing techniques, such as passive neutron and gamma measurements and neutron activation analysis, it is difficult and time consuming to detect and quantify these hazardous materials when they are contained within heavy equipment (i.e., steel pipes with 1/2" thick walls). The gaseous diffusion plant at the K-25 Site at Oak Ridge contains over 100 acres of heavy equipment used for separating uranium isotopes. Similarly, the Fernald Site has buildings and equipment used in processing uranium ore. Rapid in situ analysis of these types of equipment for hazardous elements is needed to improve the efficiency and safety of D&D efforts.

TECHNOLOGY DESCRIPTION

The K-edge technique provides an improved method for detection and quantification of heavy metals, such as Hg, U, Pu, located inside containers and equipment. An X-ray transmission measurement of the K-shell absorption edge of these materials is implemented in this task. This method provides accurate quantification of these elements regardless of container material and geometry. Typical accuracy of 10% for 10 mg/cm² of heavy metals in one inch of steel (100 ppm) is achievable. Figure 4.3-1 shows an example of a K-edge absorption spectrum for 11 mg/cm² U inside a steel pipe with 1/2" thick walls. A fieldable prototype instrument is being developed, and will be tested at DOE sites in support of the D&D Focus Area.

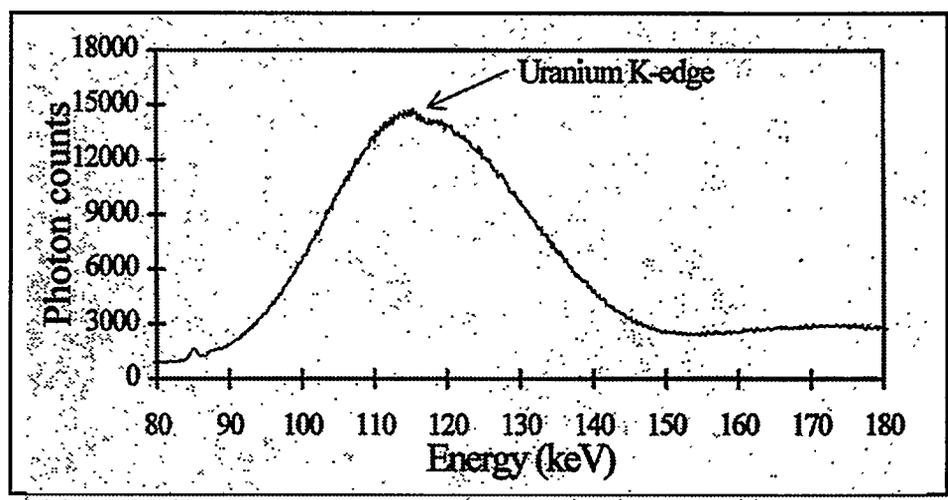


Figure 4.3-1. K-edge absorption spectrum for uranium in a steel pipe.

BENEFITS

A fast in situ method for quantifying the presence of uranium, plutonium, and RCRA-listed heavy metals inside closed containers would greatly enhance the safety and efficiency of D&D efforts. In particular, there are residual deposits of uranium found in gaseous diffusion plant equipment and in ore refining facilities. Not having to dispose of process equipment as high-level waste would yield significant savings. Accurate determination of the level of hazardous metals present would enhance the safety of dismantling operations.

COLLABORATION/TECHNOLOGY TRANSFER

This project is currently being carried out at Iowa State University and Ames Laboratory, taking advantage of existing expertise at the Center for Nondestructive Evaluation. In development of the prototype instrument, we have worked with several companies to produce specialized components. Based on this work, we anticipate further collaboration with industry to optimize equipment to meet the needs of the technique.

ACCOMPLISHMENTS

- Measurement of 1.3 μm (2.5 mg/cm²) gold in 1/2-inch steel
- Measurement of 2 μm (4 mg/cm²) uranium in 1-inch steel
- Measurement of plutonium in vitrified sample
- Prototype fieldable instrument designed

TTP INFORMATION

Portable X-ray, K-edge Heavy Metal Detector technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. CH15C251 "Portable X-ray, K-edge Heavy Metal Detector"

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4.4

ACCELERATED FACILITY CHARACTERIZATION PROCESS DESCRIPTION

TECHNOLOGY NEEDS

With the increased needs of Federal agencies and regulators to accelerate the facility characterization activities and final D&D across the DOE complex, there is a growing need to broaden the approach to facility characterization. The objective of the Accelerated Facility Characterization (AFC) process is to provide a more efficient, scientific, innovative, and integrated approach to characterize nuclear and non-nuclear facilities.

TECHNOLOGY DESCRIPTION

An innovative approach to facility characterization is being developed that integrates all appropriate scientific disciplines and characterization approaches to provide more cost- and time-effective characterization of facilities. Fundamental to the AFC process is a multi-disciplinary team approach to problem solving. Facility characterization is accelerated by working smarter to address the characterization problem efficiently by using all available information and decision tools to avoid blindly collecting un-needed data. Efficient decision making implies an intimate working relationship between the planner, sampler, analyst, data interpreter, and decision maker. The AFC process encompasses the following elements and general flow: 1) identify and assemble team; 2) define the problem; 3) develop dynamic work plan for each characterization element; 4) execute characterization; and 5) reporting.

BENEFITS

The application of the AFC process will significantly reduce costs and time, obtain more accurate, rapid information, and allow better planning of facility D&D activities.

COLLABORATION/TECHNOLOGY TRANSFER

Argonne's role will be to provide technical expertise and guidance in the application and implementation of the AFC process to characterize the facilities across the DOE complex. We are collaborating with other sites, and private sector D&D contractors. This project is jointly funded and closely coordinated with the D&D Focus Area.

ACCOMPLISHMENTS

- The AFC project received funding in January 1996. We initiated development of the work plan, and assembled the project team in February 1996. The project work plan has been completed and was delivered in March. Development of the AFC process and demonstration activities were conducted in 1996.

TTP INFORMATION

Accelerated Facility Characterization (AFC) Process Description technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. CH26C251 "Accelerated Facility Characterization (AFC) Process Description"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

None available at this time.

5.0

PROJECTS FOR THE LANDFILL STABILIZATION FOCUS AREA

The key characterization problem areas needing innovative technologies for the Landfill Stabilization Focus Area (LSFA) include: verification of proper emplacement of barriers and their subsequent integrity over time; validation that measurements taken on soil, soil gas and groundwater samples are representative of actual conditions in the subsurface; and location of buried waste, objects and structures.

Four technologies are currently under development within the Characterization, Monitoring and Sensor Crosscutting Program (CMST-CP) and many other technologies have been demonstrated and are undergoing commercialization or implementation at U.S. Department of Energy (DOE) sites to address two of these problems. The third problem, monitoring of the emplacement and long-term integrity of barriers, will be a new focus of this program beginning in FY97.

Technologies under development for locating buried waste and objects include a miniaturized electromagnetic sensor integrated into a four foot remotely piloted airplane for more cost-effective deployment and a radiometric algorithm for improved performance from aerial surveys.

For improved field analysis of soil and groundwater samples for contaminants, technologies under development include: Secondary Ion Mass Spectroscopy (SIMS) for volatile and semi-volatile organic compounds; and an advanced Inductively Coupled Plasma Mass Spectrometer for improved analysis of hazardous metals and radionuclides.

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5.1

REMOTELY PILOTED VEHICLES AND MINIATURIZED SENSORS

TECHNOLOGY NEED

The idea of using remotely piloted vehicles for aerial photography and remote sensing is not new. But many of the current aerial platforms, most of which were developed for military applications, are complicated to operate and expensive to maintain, consequently of little use in environmental restoration.

This technology adapts ordinary, readily available, model airplanes and helicopters that cost less than a thousand dollars, can be flown by any radio-control hobbyist, yet can carry a 5-10 lb sensor payload.



Figure 5.1-1. As originally constructed, this modified "Telemaster" was built to carry a 35 mm camera. Currently, we are working to add GPS autopilot, data telemetry and geophysical sensors.

TECHNOLOGY DESCRIPTION

Remote sensing techniques, such as aerial photography, multispectral scanning, and airborne geophysics, are of unquestioned value for hazardous waste site characterization, facility monitoring, and clean-up verification. But remote sensing is often dismissed as too expensive unless the waste site is large enough to justify the system mobilization and data processing costs. The goal is to demonstrate that for small sites, a radio-controlled airplane or helicopter can be used to collect high-quality data quickly and cheaply (see Figure 5.1-1).

For example, when new buildings or roads are constructed at an active disposal site, existing aerial photographs become dated, making it more difficult for the facility manager to plan further work. But by using a small, radio-controlled airplane, equipped with an ordinary 35 mm camera and a video viewfinder, a new aerial photograph of the site can be taken immediately, eliminating the cost and inconvenience of hiring a helicopter or fixed-wing aircraft. With minimal effort, a whole series of aerial photographs could be taken to document activities at the burial ground.

Task efforts are not limited to photography. A new generation of lightweight, low-power sensors is being developed by the Office of Science and Technology, including magnetometers and electromagnetic sensors. These new sensors offer exciting new applications for airborne miniature platforms.

BENEFITS

Our current efforts are focused on equipping a model plane with a miniature magnetometer, similar to those currently used by geophysicists in land-based surveys to look for buried drums and waste trenches, and a Very Low Frequency (VLF) electromagnetic sensor being designed by the United States Geological Survey (USGS). Radiation sensors and chemical vapor monitors are examples of other sensors which may be added in the future.

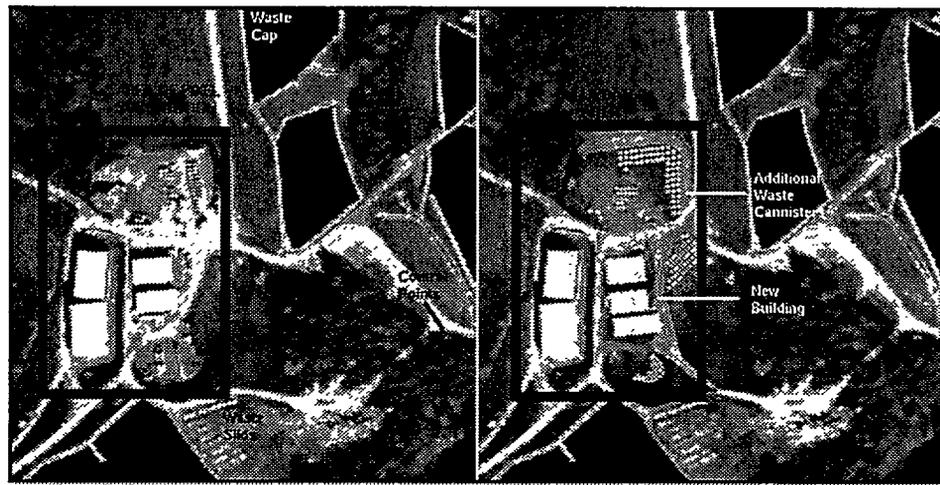


Figure 5.1-2 Aerial photographs of Solid Waste Storage Area 6 on the Oak Ridge Reservation. The photograph on the left is out-of-date; the boxed area has changed since this photograph was taken in 1990. The photograph on the right has been updated using an aerial photograph taken with the plane pictured in Figure 5.1-1. Using commercially available software, the boxed area has been digitally substituted into the older photograph to produce an updated aerial photograph.

COLLABORATION/TECHNOLOGY TRANSFER

There has been considerable interest in this project expressed by both the Office of Environmental Restoration (EM-40) workers and model aircraft manufacturers. We are currently collaborating with researchers at the USGS, Georgia Tech, BAI Aerosystems, Geophex, Brigham Young University, and the University of Texas, Arlington. A special session is being organized at the July 1996 meeting of the Association for Unmanned Vehicle Systems International (AUVSI).

ACCOMPLISHMENTS

Figure 5.1-2 shows a 1000 x 1000 ft section of an aerial photograph taken in 1990 of Solid Waste Storage Area 6, an active burial ground on the Oak Ridge Reservation. Since then, a new building has been constructed. We used the plane shown in Figure 5.1-1 to take a new aerial photograph; this newer image was then rectified and substituted into the digital version of the original aerial photograph. The results are shown in Figure 5.1-2.

TTP INFORMATION

Remotely Piloted Vehicles and Miniaturized Sensors technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. OR15C241 "Remotely Piloted Vehicles and Miniaturized Sensors"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

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5.2

ANALYTICAL SUPPORT OF AERIAL FLYOVERS CONDUCTED BY ANOTHER AGENCY

TECHNOLOGY NEED

In order to measure environmental changes and signatures of nuclear weapons production over time, a multi-temporal approach is necessary. In this application, it is critical that different types of data be spatially registered, calibrated, and compiled into a common format in order to make accurate observations. A computerized digital image processing system will be used for the analysis and visualization of data acquired in this project and from existing archives. The system includes functions for image processing, geographic data processing, and relational database operations. New algorithms and processing models for radiometric calibration and automatic signature recognition will be developed and implemented on the system.

TECHNOLOGY DESCRIPTION

The purpose of this project is to identify spectral and temporal signatures that can be used for environmental characterization at DOE sites and to develop analytical techniques for identifying environmental indicators of special nuclear materials production.

Aerial Multispectral data has been acquired over select targets at the Savannah River Site yearly as part of classified and standard DOE projects. The focus of these collection efforts are short and long term signatures that can be exploited for environmental and counter-proliferation purposes. Identification of signatures associated with the production and reprocessing of nuclear materials is an important part of that focus.

It is very difficult to identify clandestine nuclear weapons production facilities directly, but there may be environmental indicators that would suggest their existence. Those indicators are related to the environmental effects of hazardous waste disposal and/or thermal discharge. Coincidentally, these same factors are a major concern for environmental restoration at DOE facilities.

The "spectral signature" of features is determined by the unique reflectance and emittance patterns that can be discriminated in each of the channels. Multispectral imagery must be calibrated before quantitative radiometric signatures can be correlated. There exists a large archive of uncalibrated historical data that could be invaluable for monitoring temporal changes if a technique could be developed for absolute or relative calibration.

In addition to radiometric calibration, this effort will focus on the detection and characterization of buried wastes and underground storage tanks. The detection of soil disturbances resulting from burying objects with visible, reflective infrared and thermal infrared sensors depends on many surface and subsurface characteristics. These factors interact and change in relative importance, making the net effect difficult to predict. In addition, the potential range of target versus background conditions makes it extremely difficult to predict discrimination accuracy or provide a generalized solution to the problem.

The F and H areas of the Savannah River Site and associated burial grounds will be the primary focus area for this study.

BENEFITS

Any new processing technique that can take advantage of remotely sensed data can reduce costs and minimize the time required to complete ground-based environmental characterization surveys. In this specific project, the DOE can take advantage of the data that was collected over many years and by another agency and direct their support to the development of exploitation algorithms.

COLLABORATION/TECHNOLOGY TRANSFER

The results of this investigation will be briefed to DOE and to the other agencies cooperating in this activity. If successful, certain portions of the results may be considered sensitive and not made available for wide distribution. All algorithms and processing models developed in this activity will be made available to DOE and participating agencies within security guidelines determined by DOE and other agencies.

ACCOMPLISHMENTS

The work for this project is in its preliminary stages and consists mostly of database identification and "proof-of-concept" demonstrations. The work so far includes:

- Identification of archived image data sets useful for this project.
- Processing and archiving of these data sets for easy retrieval.
- Collection of Geographical Information System (GIS) coverages for a regional coordinate system and identification of features within the imagery.
- Calibration of current image data using ground targets of measured (known) reflectance (via calibrated reflectance panels or "in-scene" targets).
- Calibration of archived image data by comparison with current calibrated data ("scene-to-scene" calibration, see Figure 5.2-1).

- Spatially register 1985 and 1995 image data sets (1985 was the earliest use of the Daedalus 1268 MSS scanner). Use of image collected before data sets will require comparison of data from different scanners which have different characteristics and collect light in different wavebands.
- Demonstration of the capabilities of registered and calibrated multi-temporal image data sets
- Generation of graphic products illustrating methodologies and capabilities of the techniques developed.

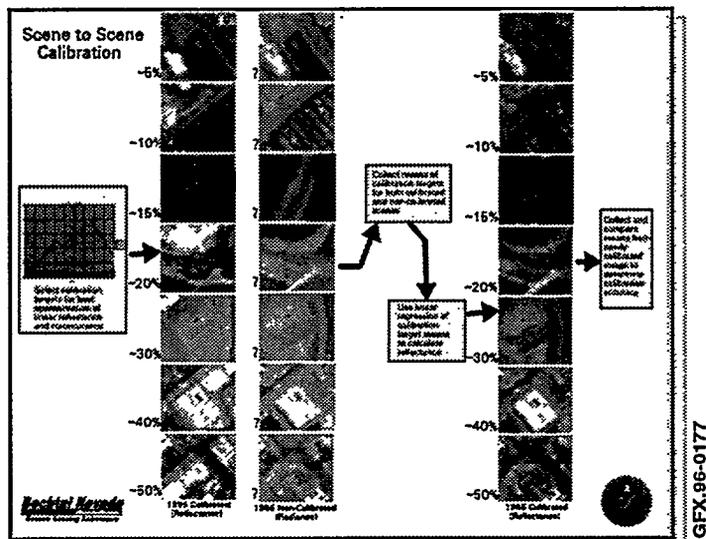


Figure 5.2-1 Scene to scene radiometric normalization for coherent change detection.

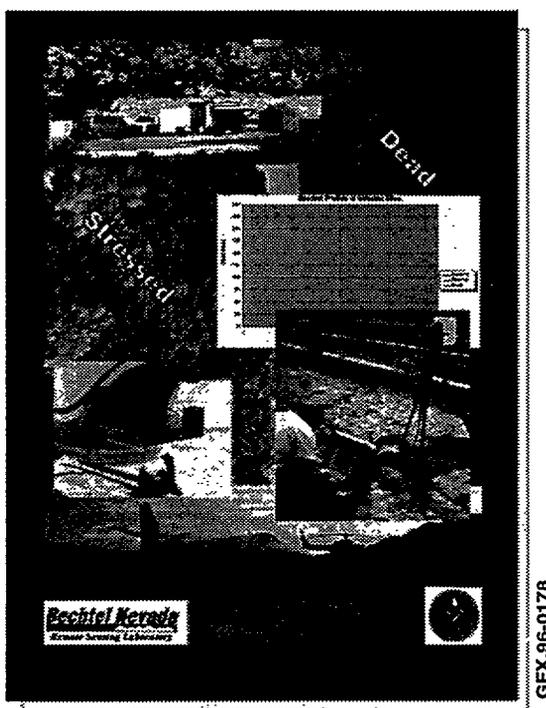


Figure 5.2-2 Simultaneous collection of airborne, ground data, and atmospheric for characterizing target phenomenology.

TTP INFORMATION

Analytical Support of Aerial Flyovers Conducted by Another Agency technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. NV00C241 "Analytical Support of Aerial Flyovers Conducted by Another Agency"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

None available at this time.

5.3

AIRBORNE AND GROUND-BASED LASER-INDUCED FLUORESCENCE IMAGING

TECHNOLOGY NEED

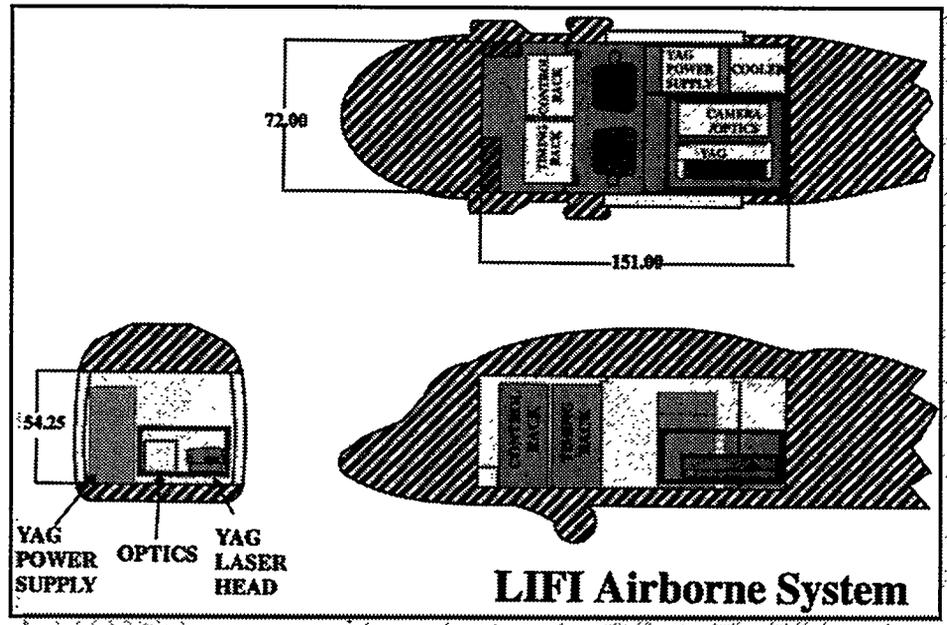
Laser-induced fluorescence (LIF) addresses the need for rapid survey tools for monitoring sites remotely, identifying contaminant "hot spots," assisting in cleanup activities, and monitoring remedial progress. Future efforts may include verification of site cleanup if regulatory sensitivity can be achieved and verified through field tests. Development and field testing of an airborne survey tool for fluorescence and reflectance signature detection promises area coverage of sites that are either spread out geographically, such as uranium firing sites, or sites that have poor access, such as clay cap areas. The concept of detecting plant stress as an indication of subsurface contamination is an active area of research at a number of federal agencies, as well as many universities. The EPCOT Land Pavilion research and development (R&D) work brings researchers together from many institutions in an effort to better understand and scope the applicability of LIF as a remote sensing tool. Laser-induced fluorescence imaging (LIFI) applications include the detection of: uranium (as uranyl oxides) during Decontamination and Decommissioning (D&D) activities; surficial heavy metals and volatile organic compounds (VOCs) (solvents, polyaromatics, and fuels) associated with landfills; and vegetation stress as an indicator of subsurface contaminant plumes.

TECHNOLOGY DESCRIPTION

LIF is an optical technique that exploits the detection of fluorescent compounds irradiated with laser light or filtered conventional light sources. Fluorescence is the prompt luminescence of a material caused by an external stimulus — in this case, a laser. When the stimulus ceases, so does the fluorescence. Common compounds which fluoresce include such organics as chlorophyll in plants and hydrocarbon fuels. When uranium is excited by a UV laser, however, its peak fluorescence is persistent (phosphorescent), lasting well longer than the laser pulse. Operationally, the prompt fluorescence of compounds which may mask the presence of uranium can be removed by delaying the activation of a photon detector 60 nsec after a laser pulse. This precise delay ensures the extinction of prompt fluorescence, effectively isolating the presence of uranium.

The scope of this TTP includes a variety of techniques to exploit LIF in several environmental applications, including aerial remote sensing (Figure 5.3-1) and hand-held portable survey tools (Figure 5.3-2) for detecting uranium on surfaces and subsurface contaminants via vegetation stress. This task has required the development of hardware, software, and analysis methods for ground-based and airborne LIFI systems. The current LIFI configurations

include UV and visible laser source (355 nm and 532 nm wavelength), intensified Charged-Coupled Device (CCD) cameras, and video monitors for instantaneous viewing. Video images can also be electronically stored for further analysis and display.



GFX.96-0176

Figure 5.3-1 Blackhawk Helicopter System



GFX.96-0018

Figure 5.3-2 Hand-Held LIFI System

This year's scope of work includes: (1) the completion of customer requested upgrades and fielding of the portable uranium survey tool at DOE sites for characterizing facility walls, floors, equipment, and surface soils; and (2) the completion and flight testing of the airborne LIFI system. The hand-held uranium survey tool will be fielded in cooperation with EM-40 personnel for D&D applications at the Oak Ridge Gaseous Diffusion Facility (K-25) and the Fernald Facility. It will also be deployed at EPCOT Center's Land Pavilion to collect data on plant stress.

The airborne LIFI system was configured last year for the DOE Convair 580T aircraft. The system has been reconfigured for helicopter usage, so that deployment is now possible on a variety of platforms, including the U-60 class (Blackhawk, Seahawk, Pavehawk), Chinooks, and SH-3s.

BENEFITS

Fluorescence techniques have the ability to detect signatures that are not observable by traditional remote sensing methods. The high spatial resolution of intensified CCD cameras and the time-resolved phosphorescence emission characteristic of the uranyl ion allow one to obtain a digital picture of the extent of surface contamination. This allows mitigation efforts to be focused on specific areas, which speeds the survey and lowers overall costs. The real-time image processing of the data into a false color composite on gray scale background allows the operator to quickly distinguish the uranium signature. Since the data is recorded on video tape, they can be reviewed for planning and evaluation of D&D activities.

The advantages of airborne systems for remote sensing are well documented. Airborne operations allow one to survey large areas in a cost-effective manner. Many DOE sites are located in remote areas, with practical access obtained only from the air. An aerial view allows identification of subtle changes and patterns that are not apparent from ground-based operations. High resolution imaging techniques under development allow one to obtain a picture of the extent and location of surface contamination. This allows mitigation efforts to be concentrated on specific local areas.

Participation with EPCOT Center in plant studies affords the opportunity to collaborate with world class plant physiologists to study the effects of plant pathogens and contamination. A variety of sensors will be used and compared to evaluate the concept of plant stress. EPCOT Center will act as a focal point for collaboration across agency boundaries and act as a site for continued collaboration. The development of robotic systems will provide platforms for testing the concept of LIF on sites of agricultural interests.

COLLABORATION/TECHNOLOGY TRANSFER

The LIF project has often used the leverage of collaboration to control costs, especially in joint agency field exercises. Efforts with EPCOT scientists have involved scientists from the DOE Remote Sensing Laboratory, DOE Special Technologies Laboratory, Army Topographic Engineering Lab (Army Corps of Engineers), and Rochester Institute of Technology. Field tests have been performed in collaboration with the above-mentioned federal agencies, members of EM-50 and EM-40 at the Oak Ridge reservation, and EM-50 personnel at Savannah River. FY96 field tests at the Oak Ridge Gaseous Diffusion Facility will be completed in collaboration with EM-40 at K-25.

An agreement to conduct sensor R&D for plant stress detection at EPCOT with a NASA-funded company, Aerodyne, has been developed. FY96 technology transfer activities include the commercialization of a disk interface card with SYSTEMWARE, a disk manufacturer in Westlake Village, CA.

ACCOMPLISHMENTS

- The hand-held LIFI system has been deployed at the K-25 Gaseous Diffusion Facility in Oak Ridge, TN, to detect uranium during D&D operations; the K-25 uranium cylinder storage yards (E and K) to detect uranium on surfaces; and EPCOT Land Pavilion to detect chromium induced stress in plants. The system will also be deployed at the Fernald Facility for a D&D demonstration this year.
- Significant improvements have been made to the hand-held system, including the addition of removable hard drives for increased data storage, expansion of digital LIFI data to 16 bits for greater radiometric resolution, integration of a companion analysis system for rapid data evaluation, and addition of a variable gate and delay laser control for greater flexibility of adjustments by the user.
- The airborne LIFI system has been reconfigured for flight testing on a U.S. Army Blackhawk helicopter at the Yuma Proving Grounds and the Los Alamos National Laboratory late in 1996. All equipment pallets have passed preliminary flight approval from the Army. A lidar system has been added for altitude correction measurements. The final camera configuration is in progress and will be completed prior to the flight tests.
- At the EPCOT Land Pavilion, laboratory facilities have been completed and plant experiments have begun. A DOE scientist is at EPCOT full-time conducting experiments. The hand-held LIFI system was deployed at EPCOT in March, with a second data collection scheduled for April. Plans were approved for a robotic system to automatically detect plant stress in the Land Pavilion. The robot has been selected and ordered and the initial sensor suite has been determined.

TTP INFORMATION

Airborne and Ground-based Laser Induced Fluorescence for Environmental Monitoring technology development activities are funded under the following technical task plan (TTP):

TTP No. NVO5C253 "Airborne and Ground-based Laser Induced Fluorescence for Environmental Monitoring"

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5.4

THREE-DIMENSIONAL THREE-COMPONENT SEISMIC IMAGING FOR SITE CHARACTERIZATION

TECHNOLOGY NEED

This technology addresses the overall need to expedite site characterization with nonintrusive methods and is applicable to the Plumes and Landfill Focus Areas as well as the Innovative and Crosscutting Programs. Typical applications are characterizing the hydrogeologic framework (e.g., bedrock channels, clay layers, faults, fractures, and porosity) that controls contaminant transport and fate, identifying soil or waste heterogeneity and integrity, and defining and delineating trench and pit boundaries.

The Technology Need Assessment report details site-specific needs throughout the DOE complex. The U.S. Department of Defense (DoD), the Environmental Protection Agency (EPA), and other government entities also require the best available technologies to conduct characterizations that can supply data for input into Records of Decision.

TECHNOLOGY DESCRIPTION

Higher resolution and additional information about the subsurface is possible with combined one-component (1C) compression-wave and two-component (2C) shear-wave data (i.e., three-component [3C] data), as compared to only a single component of data. Because the shear-wave velocity of most subsurface materials is less than the compression-wave velocity and because the dominant recovered frequencies are similar for both wave types in many areas, shear-waves are able to map much thinner features. In addition, 3C data allows determination of anisotropy. Anisotropy, which is defined as variations of a physical property depending on the direction in which it is measured, suggests that features resulting from forces other than regional geologic structure (i.e., faults and fractures) may be present in a volume. These features may include preferred grain orientation, periodic layering, and depositional or erosional lineation, and may be correlatable to preferential contaminant transport pathways.

Surveys with three-dimensional (3D) seismic methods allow investigation of a volume when surface access may be restricted because of high contamination levels. With the 3D/3C seismic method, data acquired along separate source and receiver lines outside a restricted volume provide information that can be interpreted for zones within the restricted volume. 3D seismic data can be processed so that selected profiles within a volume may be viewed from any angle and specific time or depth horizons may also be displayed and interpreted.

Given restricted entry into contaminated areas and the high cost of well completion, 3D/3C seismic technology can be a valuable means of nonintrusively characterizing hydrogeologic framework and siting monitoring wells. Other applications include determining soil or waste heterogeneity and integrity, and defining and delineating trench and pit boundaries. A full-scale demonstration will enable the 3D/3C seismic technology to be developed to a point where it can be transferred to private industry and applied at numerous suitable sites.

BENEFITS

The 3D/3C technology has three primary benefits over the baseline 2D/1C and 3D/1C technology: (1) improved characterization, (2) reduced health and environmental risks, and (3) reduced costs. A 3D/3C seismic survey will allow a uniform 3D investigation of an area, thus minimizing the possibility that the area will need to be resurveyed because of less-than-optimum placement of 2D survey profiles. This technology minimizes the number of times an area must be accessed for surveying and maximizes the amount of information possible.

COLLABORATION/TECHNOLOGY TRANSFER

The joint participants in this task, representing DOE, the private sector, academia, and another government agency, have collaborated on the common goal to develop feasible near-surface 3D/3C seismic technology. Emphasis has been placed on providing technology to the private sector that is suitable for near-term application to specific DOE EM programs. Bay Geophysical Associates, Inc., the private sector joint participant, has gained sufficient knowledge from this project to become a leader in the commercialization of the technology. The final report represents accomplished work and will be a vehicle for the transfer of this technology.

ACCOMPLISHMENTS

- Acquired baseline surface and borehole data in FY94 at Savannah River Site (SRS)
- Completed surface 2D/1C and surface-to-hole analyses. Published report in FY95
- Developed 3D/3C seismic processing software and conducted data analyses in FY95/96
- Published 3D/3C Seismic Technology Baseline Report in FY96

Figure 5.4-1 presents a graphical representation of reflection midpoints and the subsequent subsurface coverage of the 3D/3C method. Seismic energy was generated at 13 source points along Line A and received by 24 geophones

along Line C. In an area of relatively flat dip (as at SRS), the midpoint between the source and receiver is taken as the subsurface reflection point. Reflection midpoints for geophone numbers 1 and 24 and sources 1 through 13 are highlighted. The shaded area in Figure 5.4-1 represents the total subsurface coverage of all 13 sources and 24 geophones. A section line comprising any combination of sources and receivers can be displayed and interpreted. Thus, 3D seismic surveys allow investigation of an area when access may be restricted. For example, portions of the shaded subsurface coverage area may have restricted access because of high contamination levels, but 3D seismic data can still be acquired for interpretation from within that restricted area.

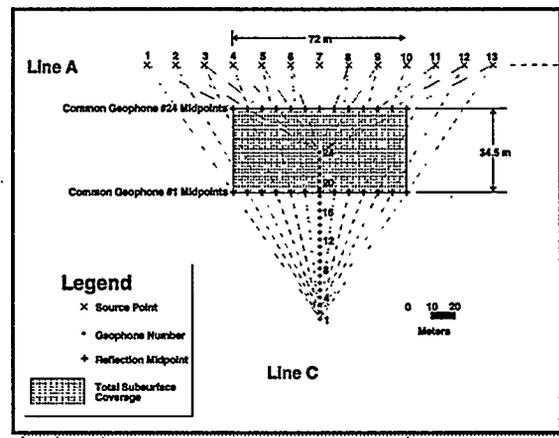


Figure 5.4-1 Three-dimensional reflection seismic coverage (shaded area). Reflection midpoints are highlighted for geophone numbers 1 and 24, sources 1 through 13.

Compressional-wave (P-wave) and shear-wave seismic time sections for common geophone midpoints 4 through 15 were converted to depth by applying velocities and static corrections, and the predominant reflectors were digitized. Figure 5.4-2 presents a 3D representation of the P-wave reflectors. Geologic horizons corresponding to a calcareous sandstone layer, the Green Clay, and the Ellenton Clay were interpreted using synthetic seismograms and depths from drilling logs

for surrounding boreholes. Each one of these geologic horizons acts as an aquiclude in the survey area. Note that the upper two reflectors are absent in relatively large areas, while the lower reflection is also absent in one localized area. The interpreted topography and the presence or absence of geologic horizons indicate possible pathways for contaminants. For example, a contaminant above the calcareous sandstone layer could conceivably migrate down through the Green Clay and the Ellenton Clay aquicludes into the underlying aquifer.

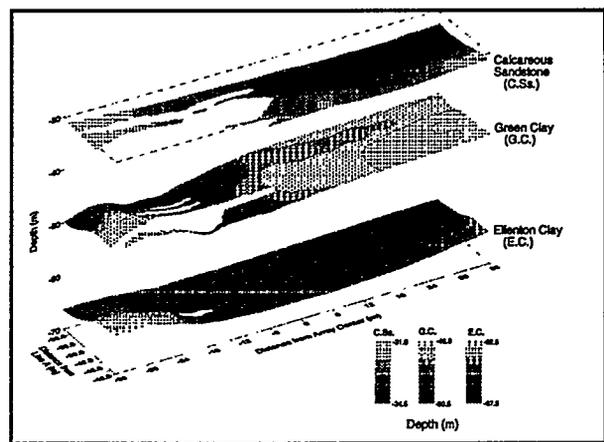


Figure 5.4-2 P-wave seismic reflectors for a portion of a shaded subsurface coverage area shown in Figure 5.4-1. Note varied topography and presence or absence of interpreted geologic horizons.

TTP INFORMATION

3D/3C Seismic Imaging for Site Characterization technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. AL94C242 "3D/3C Seismic Imaging for Site Characterization"

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5.5

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY FOR ANALYSIS OF MICROLITER SAMPLES AND SOLIDS

TECHNOLOGY NEED

This project will provide analytical technology needed to support a wide variety of remediation problems, such as: (1) real-time measurement of transuranic elements and other radionuclides, (2) rapid measurement of RCRA metals in a wide variety of aqueous or organic solutions, and (3) removing the general need for sample dissolution for accurate quantitative determination of metals. The overall cost of such analyses will also be reduced because the amount of radioactive waste samples will be reduced to microliter quantities or less, which greatly simplifies containment concerns.

TECHNOLOGY DESCRIPTION

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is already a highly sensitive and selective method for elemental and isotopic analysis. This project will investigate the ability of a microscale nebulizer called a monodisperse dried microparticulate injector (MDMI), to improve the sensitivity, speed, accuracy, and precision of ICP-MS for determination of stable elements and radionuclides.

Essentially, a micropump creates uniform wet droplets that are dried carefully and then introduced into the plasma for conversion into atomic ions. There is little or no waste solution; 100% of the sample reaches the plasma. Exposure to radioactivity and waste cleanup problems during analysis will also be greatly reduced because the nebulizer requires only nanoliter to microliter volumes of solution.

Specifically, two related projects are under study: (1) direct analysis of very small solution volumes, and (2) on-line calibration for laser ablation ICP-MS, so that solids can be analyzed directly with better accuracy than is now achievable.

The analytical capabilities of MDMI-ICP-MS, such as detection limits and tolerance to concentrated sample matrices, will be evaluated thoroughly for real samples of interest in waste remediation. This sample introduction technology is potentially applicable to existing ICP-MS devices used for analyses that support waste clean-up. It should also be suitable for field use with a mobile ICP-MS device in a van.

BENEFITS

The major benefits are more sensitive measurement of radionuclides and stable elements with little waste solution, and direct analysis of solids with simple, accurate calibration procedures that do not require matrix-matched standards.

COLLABORATION/TECHNOLOGY TRANSFER

The MDMI is an advanced prototype donated by Perkin-Elmer SCIEX. They intend to offer the MDMI as a commercial product and are eager to collaborate with us to evaluate its suitability for these special applications. The Principal Investigator has been associated with SCIEX since the early days of ICP-MS (~1982).

ACCOMPLISHMENTS

This project began in FY95. The main accomplishments to date are the following:

- Detection limits are approximately 0.1 fg of uranium in a solution volume of 0.1 nL. This represents 250,000 atoms of uranium. Detection limits are similar for most other elements
- Improvements in precision from ~2% to 0.1% relative standard deviation for measurement of ion ratios in solids by laser ablation ICP-MS
- Fundamental characterization of matrix interferences and substantial operational improvements in the reliability and consistency of MDMI-ICP-MS

Initial feasibility experiments on calibration of laser ablation ICP-MS with solution aerosols are underway.

TTP INFORMATION

Inductively Coupled Plasma-Mass Spectrometry for Analysis of Microliter Samples and Solids technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. CH15C241 "Inductively Coupled Plasma-Mass Spectrometry for Analysis of Microliter Samples and Solids"

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Allen, L. A., H.-M. Pang, A. R. Warren, and R. S. Houk. "Simultaneous Measurement of Isotope Ratios in Solids by Laser Ablation with a Twin Quadrupole Inductively Coupled Plasma Mass Spectrometer," *J. Anal. Atomic Spectrom.*, 10, 267-271 (1995).

5.6 SECONDARY ION MASS SPECTROSCOPY ANALYSIS

TECHNOLOGY NEED

DOE has many contamination problems requiring the determination of contaminants that adhere tightly to waste, environmental, and industrial surfaces. There is a critical need in DOE and industry for characterization technologies that are fast, inexpensive, and can address surface contamination. An excellent example of this need is the detection of mercury on soil samples, and equally important, the identification of mercury species present. The mercury speciation issue is important because differing environmental mobility among the species alters risk assessment associated with mercury contamination. For example, mercury present as $\text{Hg}(\text{NO}_2)_3$ is highly mobile and would require containment; on the other hand, mercury present as HgO strongly adsorbs to soil and poses a much lower risk. At the present time, there is no facile means to make a distinction between these species on soil samples. See Figure 5.6-1.

Another example of this need is characterization of core and particulate samples from radioactive waste in underground storage tanks, which currently costs an average of \$750,000/core analysis. Technologies capable of determining chemical speciation are needed to reduce the number of analyses needed, and to improve the estimation of tank energy content (critical for risk assessment associated with tank characterization and remediation activities).



Figure 5.6-1 Depiction of SIMS Bombardment of Hg-Contaminated Soil

TECHNOLOGY DESCRIPTION

Fast, inexpensive, and non-polluting instrumentation for the detection of surface contaminants is being developed at the Idaho National Engineering Laboratory (INEL) using advanced Secondary Ion Mass Spectroscopy (SIMS) technology. The attributes of this technology make it extremely attractive for waste and environmental characterization:

- No sample preparation is required
- No waste is generated

- Analysis is rapid and simple
- Capable of speciation, "fingerprinting"
- Amenable to almost any sample type
- Amenable to involatile organics, salts

SIMS has a simple principle of operation: surfaces are bombarded with high-energy particles, which "sputter" the contaminants into the gas-phase, where they can be detected as ions.

The objective of the SIMS analysis program is to develop instrumentation and chemical applications for the detection of chemical species, identification of semivolatile, involatile, or adsorbed contaminants on the surfaces of soils, minerals, salts, rocks, and other difficult to handle sample types. During the course of the SIMS analysis program, detection applications and instrument development were accomplished. In FY96, the objective of the program is to transfer technology to end users and to instrument manufacturers.

BENEFITS

New analytical capability, reduced analysis cost, and technology transfer are among the benefits of the SIMS Demonstration Program. Since the technology requires no sample preparation, is rapid, and generates no waste, lower analytical cost can be realized. The technology also provides a facile approach toward the analysis of involatile contaminants, which are difficult to analyze using current methods and instrumentation: organophosphate and hazardous metal species are examples of classes of chemicals which are amenable to the SIMS characterization approach. The program has also resulted in the transfer of software components to instrument manufacturers, and the transfer of hardware components is expected in the near future. The development of the transportable ion trap SIMS instrument has resulted in a device which can be used in the field for on-site characterizations. Instruments that are based on the OTD-funded prototype are being constructed for other government users.

COLLABORATION/TECHNOLOGY TRANSFER

Technology transfer has been pursued with three vendors. Given the nature of the technology, the focus of the technology transfer activities has been on transfer of SIMS components, instead of a complete instrumental package, which would require the manufacturer to engineer it's instrument from scratch. A license was completed for data acquisition and instrument control software with Extrel (Pittsburgh, PA). Transfer of the primary ion gun technology to Phi-Evans, Inc. (Redwood City, CA) has been actively pursued. This activity requires a head-to-head comparison of existing ion guns with the INEL ReO₄-

gun. It is expected that this activity will be completed by May 1996, where upon negotiations for transfer of ion gun technology will be renewed with Phi-Evans.

Figure 5.6-2 is a schematic diagram of a prototype ion trap SIMS instrument being developed at INEL. The instrument is capable of anion and cation acquisitions, and enhanced selectivity and sensitivity will result from MS/MS and selective ion storage capability. The capability of the instrument has resulted in a DOD end user (U.S. Army Chemical Material Destruction Agency, Non-Stockpile Program), who is funding fabrication of second generation prototype ion trap SIMS instruments. This development has motivated negotiations with Teledyne (Mountain View, CA, an ion trap vendor), for the purpose of transferring SIMS components, thereby providing the end user with a commercial technology vendor.

ACCOMPLISHMENTS

The rapid analysis of simulated salt cake samples was demonstrated using the laboratory-based SIMS instrument located at the INEL. The analyses required no sample preparation, and hence required less than 10 minutes; in addition, no waste was generated. A unique attribute of our R&D 100 Award-winning, pulsed-extraction SIMS instrument is the ability to analyze cations and anions at the same time. This attribute is especially valuable for salt cake analyses because the salt samples contain both anion and cation species. Nitrite, nitrate, cyanide, and hydroxide anions, and iron, sodium, potassium, and nickel complexes were detected.

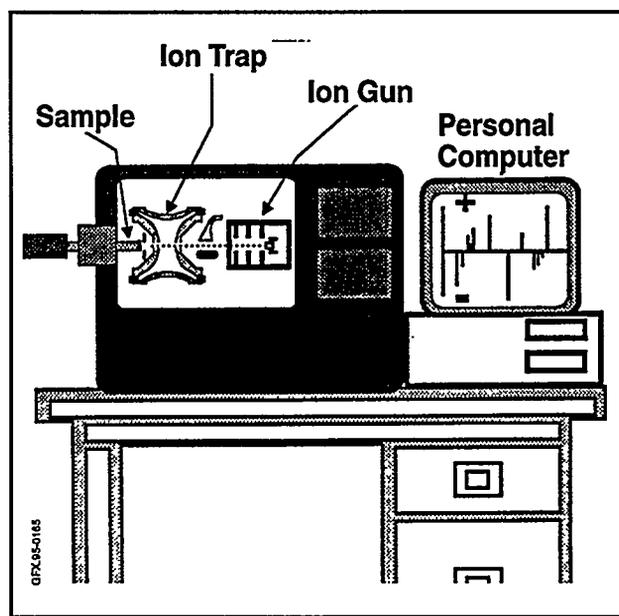


Figure 5.6-2 Schematic diagram of prototype ion trap SIMS instrument being developed at INEL.

Since demonstrating SIMS for the characterization of salt cake, the SIMS analysis has been redirected toward the determination of metal speciation on soil samples. Research conducted in FY95 using SIMS showed that different mercury species could be distinguished by forming surface derivatives, which is easily accomplished using simple organic acids and bases. The mercury surface derivatives were specific for the inorganic mercury species originally present, and were easily detected using an ion trap SIMS instrument (see Figure 5.6-2).

Instrument transportability, and improved sensitivity and selectivity are desired attributes of the instrumentation that will be constructed in this program. An ion trap mass spectrometer (ITMS) satisfies these requirements, and therefore an ion trap SIMS instrument was constructed in FY95. Using this instrument, it is possible to observe fragile, but species-diagnostic organometallic ions, which cannot be observed using other types of instrumentation. The instrument is also smaller in size: the current version resides on a cart which has a footprint of approximately 2 x 3 feet.

TTP INFORMATION

Secondary Ion-Mass Spectroscopy Analysis technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. ID72C241 "Secondary Ion-Mass Spectroscopy Analysis"

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Groenewold, G.S., J.C. Ingram, J.E. Delmore, and A.D. Appelhans. "Static SIMS Analysis Of Tributyl Phosphate On Mineral Surfaces: Effect Of Fe(II)," *Journal of American Soc. Mass Spectrometry*, p. 6, 165-74 (1995).

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Groenewold, G.S., A.D. Appelhans, J.C. Ingram, J.E. Delmore, and D.A. Dahl. "Surface Derivatization of Inorganic Mercury: Formation of bis(Ankylamine) Mercury Cations," *Journal of American Chemical Society*, submitted (1996).

DOE BUSINESS OPPORTUNITIES FOR TECHNOLOGY DEVELOPMENT

WORKING WITH THE DOE OFFICE OF ENVIRONMENTAL MANAGEMENT

The Office of Environmental Management (EM) provides a range of programs and services to assist private sector organizations and individuals interested in working with DOE in developing and applying environmental technologies. Vehicles such as research and development contracts, subcontracts, grants, and cooperative agreements enable EM and the private sector to work collaboratively. In FY95, 39 percent of Office of Science and Technology (OST) funding went to the private sector, universities, and other federal agencies. EM's partnership with the private sector is working to expedite transfer of newly developed technology to EM restoration and waste management organizations, industry, and other federal agencies.

Several specific vehicles address institutional barriers to effective cooperation and collaboration between the private sector and DOE. These mechanisms include contracting and collaborative agreements, procurement provisions, licensing of technologies, consulting arrangements, reimbursable work for industry, and special consideration for small businesses.

INFORMATION ON EM

The EM Center for Environmental Management Information provides the most current facts and documents related to the EM program. Through extensive referrals, the Center connects stakeholders to a complex-wide network of DOE Headquarters and Operations Office contacts.

To obtain information from the EM Center for Environmental Management Information, write or phone:

EM Center for Environmental Management Information
U.S. Department of Energy
P.O. Box 23769
Washington, DC 20026-3769
1-800-736-3282
cemi@dgs.dgsys.com

THE COOPERATIVE RESEARCH AND DEVELOPMENT AGREEMENT

The Cooperative Research and Development Agreement (CRADA) is a written agreement between one or more federal laboratories and one or more nonfederal parties through which the government provides personnel, facilities,

equipment, and other resources, with or without reimbursement, to support a shared research agenda. The nonfederal parties may also provide funds, personnel, services, facilities, equipment, intellectual property, or other resources to support the research. DOE developed a modular CRADA to be responsive to the needs of participants while protecting the interests of the government and its taxpayers. DOE also has issued the small business CRADA to expedite agreements with small businesses and other partners that meet DOE's requirements. During FY95, EM entered into more than 60 CRADAs.

THE RESEARCH OPPORTUNITY ANNOUNCEMENT

The Research Opportunity Announcement (ROA) is a solicitation for industry and academia to submit proposals for potential contracts in basic and applied research, ranging from concept feasibility through proof-of-concept testing in the field. This mechanism is used when EM is looking for multiple solutions for a given problem. ROAs are issued annually by EM. The EM ROA provides multiple awards and is open all year. ROAs are announced in the *Commerce Business Daily*, and typically published in the *Federal Register*.

For questions on ROAs, contact:

Robert Bedick
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(304) 285-4505

To learn about EM Technology business opportunities, connect to the METC Homepage:
<http://www.metc.doe.gov/business/solicita.html>

THE PROGRAM RESEARCH AND DEVELOPMENT ANNOUNCEMENT

EM uses the Program Research and Development Announcement (PRDA) to solicit proposals from nonfederal parties for research and development in areas of interest to EM. The PRDA is used for projects that are in broadly defined areas of interest where a detailed work description might be premature. It is a tool to solicit a broad mix of applied research, development, demonstration, testing, and evaluation proposals.

For questions on PRDAs, contact:

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To learn about EM Technology business opportunities, connect to the METC
Homepage:
<http://www.metc.doe.gov/business/solicita.html>

THE SMALL BUSINESS INNOVATION RESEARCH PROGRAM

The Small Business Innovation Research (SBIR) Program promotes small business participation in government research and development programs. This legislatively mandated program is designed for implementation in three phases from feasibility studies through support for commercial application. DOE publishes solicitation announcements through the Small Business Innovation Research Office each year to define research and development areas of interest.

For further information about SBIR programs, contact:

SBIR Program Manager
U.S. Department of Energy
Small Business Innovation Research Program
ER-33
19901 Germantown Road
Germantown, MD 20874-1290
(301) 903-5707
sbir_sttr@mailgw.er.doe.gov

BUSINESS AGREEMENTS

Cost-Shared Contracts

Nonfederal parties working under DOE contract can agree to share some of the cost of developing a technology for a nonfederal market. This arrangement may involve cash, in-kind contributions, or both.

Grants and Cooperative Agreements

These contractual arrangements provide the recipient with money and/or property to support or stimulate research in areas of interest to DOE. DOE regularly publishes notices concerning grant opportunities in the *Commerce Business Daily*.

Research and Development Contracts

This acquisition instrument between the government and a contractor provides supplies and services to the government. DOE may enter directly into research and development contracts, and DOE laboratories and facilities can subcontract research and development work to the private sector. Announcements on requests for proposals are published in the *Commerce Business Daily* and are available through the EM Homepage on the Internet: www.em.doe.gov

Licensing Technologies

DOE contractor-operated laboratories can license DOE/EM-developed technology and software. In situations where DOE retains ownership of a new technology, the Office of General Counsel serves as licensing agent. Licensing activities are conducted according to existing DOE intellectual property provisions and can be exclusive or nonexclusive, for a specific field of use, for a geographic area, United States or foreign usage. Information on licensing technologies may be obtained by contacting the Office of Research and Technology Applications (ORTA) representatives listed later in this section.

Technical Personnel Exchange Arrangements

Personnel exchanges provide opportunities for federal or DOE laboratory scientists to work together with scientists from private industry on a mutual technical issue. Usually lasting one year or less, these arrangements foster the transfer of technical skills and knowledge. These arrangements require substantial cost-sharing by industry, but DOE has an advanced class patent agreement in place for this provision and the rights of any resulting patents become the property of the private industry participant. Contact an ORTA representative for more information.

Consulting Arrangements

Consulting arrangements are formal, written agreements in which a DOE laboratory or facility employee may provide advice or information to a nonfederal party for the purpose of technology transfer, or a nonfederal party may consult with the laboratory or facility. Laboratory/facility employees participating in this exchange of technical expertise must sign a nondisclosure agreement. Contact an ORTA representative for more information.

Reimbursable Work for Industry

This concept enables DOE personnel and laboratories to perform work for nonfederal partners when laboratories or facilities have expertise or equipment not available in the private sector. Reimbursable Work for Industry is usually termed "work for others." An advanced class patent waiver gives ownership of any inventions resulting from the research to the participating private sector company. Contact an ORTA representative for more information.

Office of Research and Technology Applications

Each federal laboratory has an Office of Research and Technology Application. These offices serve as technology transfer agents for the federal laboratories. They coordinate technology transfer activities among laboratories, industry, and universities. ORTA offices license patents and foster communication between researchers and technology customers.

ORTA Representatives:

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Stanford Linear Accelerator Center

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ACRONYMS

1C	One-component
2D	Two-dimensional
3D/3C	Three-dimensional/Three-component
AFC	Accelerated Facility Characterization
ANL	Argonne National Laboratory
ARA	Applied Research Associates, Inc.
AUVSI	Association for Unmanned Vehicle Systems International
AVS	Application Visualization System
BEL	Brochfield Engineering Laboratory, Inc.
BNL	Brookhaven National Laboratory
CCD	charge coupled device
CEM	Continuous Emission Monitor
CHCs	Chlorinated Hydrocarbons
CLP	Contract Laboratory Program
CMST	Characterization, Monitoring and Sensor Technology
CMST-CP	Characterization, Monitoring and Sensor Technology Crosscutting Program
CPAC	Center for Process Analytical Chemistry (at the University of Washington)
CPG	Coplanar Grid
CPT	Cone Penetrometer Truck
CPU	Central Processing Unit
CRADA	Cooperative Research and Development Agreement
CSAMT	Controlled Source Audiofrequency Magnetotelluric
C SCT	Consortium for Site Characterization Technologies
CT	Computerized Tomography
CVD	Chemical Vapor Disposition
CZT	Cadmium Zinc Telluride
D&D	Decontamination and Decommissioning Focus Area

DIAL	Diagnostic Instrumentation and Analysis Laboratory (Mississippi State University)
DNAPLs	Dense Non-Aqueous Phase Liquids
DoD	Department of Defense
DOE	Department of Energy
DOSB	D-Area Oil Seepage Basin
DQO	data quality objectives
DST	double-shelled storage tank
DWPF	defense waste processing facility
EM	Office of Environmental Management
EM-30	Office of Waste Management
EM-40	Office of Environmental Restoration
EM-50	Office of Science and Technology
EM-60	Office of Nuclear Material and Facility Stabilization
EPA	Environmental Protection Agency
ERT	Electrical Resistance Tomography
ESC	Expedited Site Characterization
ETG	Environmental Technology Group
FFD	fuel fluorescence detector
FLAA	flame atomic absorption
FSU	Former Soviet Union
FTIR	Fourier Transform Infrared Spectroscopy
FY	Fiscal Year
GC/MS	gas chromatography/mass spectrometry
GFAA	Graphite Furnace Atomic Absorption
GIS	Geographical Information System
GPR	Ground Penetrating Radar
GW	Ground water
HCl	Hydrochloric Acid
HLW	High-Level Waste

IAG	Interagency Agreement
ICP-MS	inductively coupled plasma mass spectrometry
ICPP	Idaho Chemical Processing Plant
ICT	Innovative Characterization Technology
IIA	Innovative Investment Area
INEL	Idaho National Engineering Laboratory
ITMS	Ion Trap Mass Spectrometer
JCEM	Joint Coordinating Committee on Environmental Management
LANL	Los Alamos National Laboratory
LASS	Laser Spark Spectroscopy
LDUA	Light Duty Utility Arm
LIBS	Laser-Induced Breakdown Spectroscopy
LIF	Laser-Induced Florescence
LIFI	Laser-Induced Florescence Imaging
LLNL	Lawrence Livermore National Laboratory
LOWs	liquid observation sells
LSERs	linear solvation energy relationships
LSIT	Large Scale Infiltration Test
LSFA	Landfill Stabilization Focus Area
MDMI	monodisperse dried microparticulate injector
METC	Morgantown Energy Technology Center
MINATOM	Ministry of Atomic Energy of the Russian Federation
MSE-TA	MSE Technology Application, Inc.
MSU	Mississippi State University
MWFA	Mixed Waste Characterization Treatment & Disposal Focus Area
NAPLs	Non-Aqueous Phase Liquids
NDA	Nondestructive Assay
NDE	Non-destructive Evaluation
NFA	No Further Action

NN	neural network
OCVZ	Organic Contaminated Vadose Zone
OGI	Oregon Graduate Institute
ORNL	Oak Ridge National Laboratory
ORTA	Office of Research and Technology Applications
OST	Office of Science and Technology
OTD	Office of Technology Development
P-Wave	Compressional wave
PAWS	portable acoustic wave sensor
PC	Photo conductive
PCE	polychloroethylene
PE	Performance Evaluation
PECVD	photo enhanced chemical vapor deposited
PI	Principal Investigator
PNNL	Pacific Northwest National Laboratory
POC	Physical Optics Corporation
POLO	position locator device
ppb	parts per billion
ppm	parts per million
PRDA	Program Research and Development Announcement
QA/QC	Quality Assurance/Quality Control
R&D	research and development
RCI	Rapid Commercialization Initiatives
RCRA	Resource Conservation and Recovery Act
ROA	Research Opportunity Announcement
RTR	Real-Time Radiography
RWMC	Radioactive Waste Management Complex
SAW	surface acoustic wave
SBIR	Small Business Innovative Research
SCAPS	Site Characterization and Analysis Penetrometer System

SDx	Spectrum Diagnostix
SERDP	Strategic Environmental Research and Development Program
SIMS	Secondary Ion Mass Spectroscopy
SMDE	static mercury drop electrode
SNL	Sandia National Laboratory
SOPT	state-of-the-practice technologies
SRS	Savannah River Site
SSC	site specific contaminants
SST	Single Shell Tank
STCGs	Site Technology Coordination Groups
SVOC	Semi-Volatile Organic Compound
TCE	trichloroethylene
TCLP	Toxicity Characteristic Leaching Procedure
TDGC/MS	Time Domain Gas Chromatography/Mass Spectrometry
TDL	tunable-diode-laser
TDR	time domain reflectometry probe
TFA	Tanks Focus Area
TIE	Technical Information Exchange
TIRS	Transient Infrared Spectroscopy
TPM	Technical Program Manager
TPO	Technical Program Office
TRP	Technology Reinvestment Project
TRU	Transuranic
TSM	thickness shear mode
TTP	Technical Task Plan
TVS	Transportable Vitrification System
USGS	United States Geological Survey
USTs	underground storage tanks
UV	Ultra-Violet
VLF	Very Low Frequency

VOC Volatile Organic Compound
WETO Western Environmental Technology Office
WHC Westinghouse Hanford Corporation
WSRC Westinghouse Savannah River Company

